SOME MEASUREMENTS OF MAGNETIC DOUBLE REFRACTION

By

OLLE SNELLMAN

Uppsala 1944

Almqvist & Wiksells Boktryckeri
Aktiebolag

SOME MEASUREMENTS OF MAGNETIC DOUBLE REFRACTION

INAUGURAL DISSERTATION

BY

OLLE SNELLMAN

BY DUE PERMISSION OF THE PHILOSOPHICAL FACULTY OF THE UNIVERSITY OF UPSALA, TO BE PUBLICLY DISCUSSED IN THE LECTURE ROOM OF THE CHEMICAL INSTITUTE, ON MAY 24TH, 1944, AT 10 A. M.

UPPSALA 1944
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Preface.

The greater part of the investigations were carried out during the years 1942 and 1943 at the Institute of Physical Chemistry at Upsala University.

To the Chief of the Laboratory, Professor The Svedberg, the author wishes to express his warm gratitude for giving him facilities to perform this work.

To my late teacher Dr. Y. Björnståhl I am deeply indebted for introducing me to the interesting study of accidental double refraction.

The author wishes to thank most cordially all his colleagues for many interesting discussions in scientific things.

Part of the expenses connected with the investigations were defrayed by grants from the Rockefeller Foundation.

The author wants to express his very best thanks to Mr Grenville Grove for translating the work and to the British Council for making a grant to cover the expenses for the translation.

Upsala, March 1944.

Olle Snellman.

CHAPTER I.

The Electromagnet.

The electromagnet employed in these investigations was constructed by ASEA (Allmänna Svenska Elektriska AB.), Västerås, (designer Dr. L. Dreyfus) with the collaboration of Dr. Y. Björnståhl.

A few data regarding this electromagnet may be of interest.

Its housing consists of a cylinder with an internal diameter of 152 cm. This cylinder is firmly screwed to a bottom plate, whilst another plate forms a plunger displaceable in axial direction.

The diameter of the pole cores diminishes from 112 cm at the bottom to 59 cm at the top. The pole core is provided with a bore-hole, 20 cm in diameter, which receives a central core, adjustable by means of hand-wheels. Pole shoes and pole horns of different kinds can then be fixed on the pole cores.

The free space between the coils can be varied between 15 and 50 cm by displacing the one movable pole plate, which is guided by three strong screws and nuts. The nuts are retatable in a lid firmly screwed to the magnet housing. The pole plate is intended to receive the entire force of attraction between the poles, estimated at 60 tons.

The conductors of the coils consist of a rectangular copper tube (21×23 mm^2), with a central aperture, 10 mm in diameter, for the cooling water (about 60 litres of water per minute).

The housing of the magnet rests on a roller device, consisting in two runners, firmly screwed to the housing and running on rollers, as well as rack and pinion rotated by three-phase motor over a gearing. This device enables the magnet housing to be adjusted in a horizontal, vertical or intermediate position.

Finally, the whole magnet with its roller device can also be rotated round a turn-table with a ball-bearing ring.

The current for the magnet is supplied from a generator.

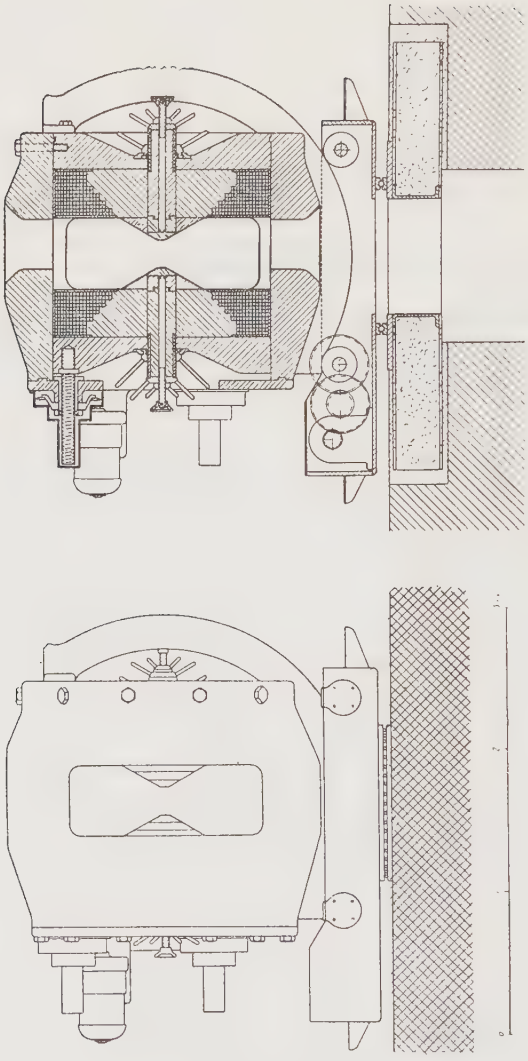

Figure 1 a and b.

The Electromagnet. (From Y. Björnståhl: The New Laboratory of Physical Chemistry at Upsala University.)

The Upsala magnet weighs 37 tons, whereas the electromagnet of the French Academy of Science, at Bellevue near Paris, (the only one whose field is of the same order of magnitude as that of the Upsala magnet), has a weight of 120 tons.

For further details about the electromagnet see Dreyfus (1) and Björnståhl (2).

CHAPTER II.

Measurements of the fields at different types of pole shoes.

For the computation of the strength of the magnetic field, the induction method was adopted. An exploring coil in connection with a flux meter was removed out of the field. Owing to the change of field, an electromotive force producing a current the strength of which can be read on the flux meter, is generated in the coil. By the use of a flux meter, in lieu of a ballistic galvanometer, one gains the advantage that the current integral is very slightly dependent on time (times under 10 sec.). In our tests, it was found that, on a very slow removal of the exploring coil from the field, the difference, as compared with rapid removal, was at most 1/4 per cent.

The arrangement of the apparatus is shown, in outline, in figure 2. The flux meter F is connected in series with the coil S and with one of the coils of a mutual induction L. By the double-contact commutator O, the current can be converted. For the purpose of calibration, there is a cell B, connected in a potentiometer system, and merely part of the voltage is used, in order to obtain a constant current. A is an ampère meter and R a resistance for better regulation of the current. K is a switch.

When the coil is removed from the field, the result is an electric »shock» and a deflection S in the flux meter. The amount of electricity which then passes through the system is Q. If a field H has been set up, and if the coil has the area A, we obtain

$$Q = CS = \frac{HA}{r}$$

where r is the resistance in the circuit. C is a constant.

$$H = \frac{rC}{A} S.$$

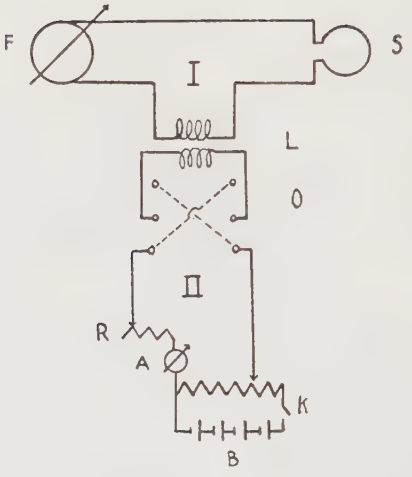

Figure 2. Sketch of Experimental Arrangements for Measuring the Field.

For the computation of the constant C, circuit II is used. When the current is closed in this circuit, the result is an electric »shock» (owing to the mutual induction). The strength of this »shock» can be estimated. If the current strength in circuit II is i and the mutual induction L, the electromotive force generated is $\frac{Li}{10}$

$$Q = CS_1 = \frac{Li}{10\,r}.$$

We thus obtain

$$H = \frac{LiS}{10\,A\,S_1}.$$

The flux meter employed was of the Grassot type. The deflection of the flux meter was read with a mirror and a curved scale. The quantity Cr was constant within the limits of error (1 ‰). As the sensitiveness of the flux meter can be modified by varying the resistance in the secondary circuit, the effect of such variation was studied.

We obtained the following figures when different resistances were connected

$$16.5\,\Omega \quad C = 130.6 \cdot 10^2$$
$$26.5\,\Omega \quad C = 132.0 \cdot 10^2$$
$$66.5\,\Omega \quad C = 137.4 \cdot 10^2$$

Thus a fully linear course according to the formula $C = k_1 + k_2 R$ was found. At very high field strengths it is sometimes necessary to shunt the flux meter. When the coil is in motion with the angular velocity ω, we have the e. m. f.

$$e = ir + C'\omega + L\frac{di}{dt}.$$

C' is the coil constant in the flux meter (depending on the area and on the field of the coil). As the directive force can be neglected, the equation of motion will be

$$D\frac{d\omega}{dt} = C'i - k'\omega = \frac{C'e}{r} - \frac{C'L}{r}\frac{di}{dt} - k'\omega - \frac{C'^2\omega}{r}.$$

D is the moment of inertia.

k' represents air damping and other such factors.

At the beginning of the current »shock» $i = 0$; $\omega = 0$

At the end » » » » $i = 0$; $\omega = 0$

and then

$$\frac{C'}{r}\int e\,dt - \left[\frac{C'^2}{r} + k'\right]\int \omega\,dt = 0.$$

This gives

$$\int i\,dt = \left[\frac{C'}{r} + \frac{k'}{C'}\right]S.$$

S = the deflection

now $k' \ll C'$. When r is small we have

$$Q = \frac{C'S}{r} = \frac{HA}{r}$$

$$H = \frac{C'}{A}S.$$

If the flux meter is now shunted we have (see figure 3)

$$r_s i_s = r_g i + C'\omega$$

$$i = i_R - i_s.$$

$$r_s i_R = r_g + r i_s + C'\omega.$$

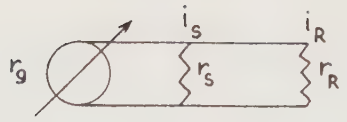

Figure 3.

Index R refers to the current strength and resistance in the external part of the circuit

s refers to the current strength and resistance in the shunt

g » » » » » » » » » » galvanometer

$$Q = \left[\frac{r_g + r_s}{r_s} \cdot \frac{k'}{C'} + \frac{C'}{r_s}\right] S$$

$$Q = \frac{HA}{r_g + r_s}.$$

For reference see Handb. d. Physik XVI p. 381 (Springer, Berlin 1927).

We can thus put

$$HA = \frac{r_s + r_g}{r_s} C' S.$$

On calibration we obtain

$$\frac{Li}{10} = \frac{r_s + r_g}{r_s} C' S_1.$$

And we get the same equation as before

$$H = \frac{Li}{10A} \frac{S}{S_1}.$$

Thus one can measure the field in the same way as before when the coil is shunted.

Coils and coil holders.

For the purpose of calibration, a coil was prepared with the greatest care. It was made of brass, carefully turned, and, when examined with a micrometer gauge, was found to have a maximum error of 0.007 mm in its radius. Its diameter was computed firstly with a micrometer screw, calibrated by a Johansson gauge, at 29.95 mm and secondly with a piece of tin-foil laid round its surface, at 29.96 mm. Under microscopic magnifica-

tion, 20 turns of insulated copper wire with a microscopically measured diameter of 0.113 mm, were then carefully wound round it. The wire was very even, the maximum difference being 2 in the third digit. The insulation was 0.001 mm in thickness. When the turns of wire had been arranged, they were coated with zapon lacquer. In order to avoid disturbances, the ends of the wires were twined together. The diameter of the coil was then assumed to be 30.07 mm. The area of this normal coil was thus 142.0 cm^2.

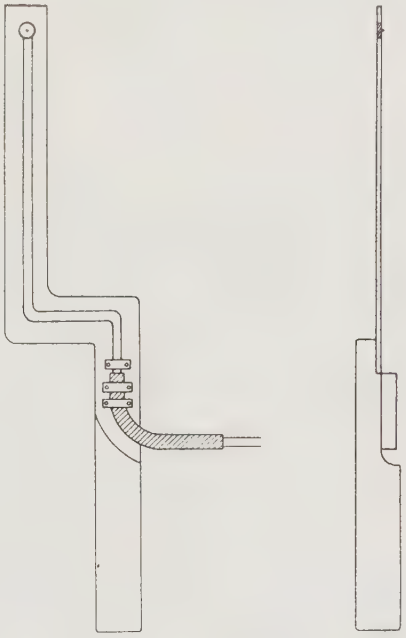

Figure 4. Coil Holder.

The other coils were calibrated against this normal coil.

The coil most used was one which was made of steatite and was 3 mm in diameter. A view of such a coil when mounted is shown in figure 4. The coil holder was securely held by an optical clamp. The coils were fixed with wax in an aperture in a brass plate. These intertwined wires were placed in a groove and coated with wax. From the coil holder the wire continued through a systoflex tube, extending beyond the actual magnet. Here, where the field was not large, the wire was tacked on to thicker wire, leading to the flux meter. In order to avoid interference from the magnetic field, the flux meter had been placed in an adjacent room. In the central aperture of the steatite disc a small brass pin serving as an adjuster for the coil was fixed.

The adjustment of the coil relatively to the centre point of the pole shoe was effected by measurement of the distances. A rod, which ends in a point, displaceable laterally and longitudinally, was first set in the zero position in the centre of the one pole shoe and was then shifted to the side of the coil.

The main coil was then compared with the steatite coil 3 mm in diameter. In these tests we used a very homogeneous magnetic field. In addition to these coils, we also tested coils with intermediate radii, and the correspondence was found to be very good.

For the two coils the following average values were obtained:

D	S	Shunt	i	$2\,S_1$
0.3 cm	139.7 mm	∞ Ω	0.0500 amp	201.4 mm
3 »	308.1 »	0.6 Ω	0.9100 »	87.20 »

The area of $D\,3$ was 142.0 cm^2.

From these results we obtained for the coil $D\,0.3$ the area 1.531 cm^2, and for the constant by which S must be multiplied in order to produce the field strength $B = 324.3$, when $L = 1.000\ 10^{-2}$ Henry.

The area was then computed also in relation to the susceptibility of the water. In this case the Quincke method was adopted. A long Jena glass tube, extending beyond the magnet, was employed. The tube was 1 mm in width at the pole shoes, otherwise 5 mm; it ended in a container with water standing on a base plate movable by a spindle.

By means of a telescope with a hair-cross reticle, the water column in the field was adjusted to the zero position, and the distance travelled by the spindle, when the change of the water-level in the tube was compensated, was read with the aid of a cathetometer.

The formula which gives the field strength, with corrections according to Piccard (3), is the following:

$$H^2 = \frac{2\,g\,h\,(1 + d^2/D^2 - \delta/\gamma)}{\chi - \chi_e\,\delta/\gamma}$$

d = outer diameter of tube
D = internal diameter of container
δ = density of the air
γ = density of the water
g = acceleration
h = distance travelled by spindle
χ = susceptibility of the water
χ_e = susceptibility of the air

We had 18° C and a pressure of 760 mm Hg

$$d = 7.7 \text{ mm} \qquad D = 96 \text{ mm}$$

$$\frac{\delta}{\gamma} = 0.00112 \qquad \frac{d^2}{D^2} = 0.00643 \quad \text{and} \quad 1 + \frac{d^2}{D^2} - \frac{\delta}{\gamma} = 1.0053$$

$\chi = -0.7199\ 10^{-6}$. As boiled-out water was not used in these tests, a correction was made for the oxygen content of the water. According to Piccard's investigation, this correction amounts to $+ 0.0009\ 10^{-6}$. For the susceptibility of the water, we thus obtain $\chi = -0.7190\ 10^{-6}$. Finally $\chi_e \delta/\gamma = +0.02904\ 10^{-6}$ and $\chi - \chi_e \delta/\gamma = -0.7480\ 10^{-6}$. From these data we obtain $H = -0.2639\ h$.

The following table shows the average values computed for five different adjustments. Between each series the field was measured with the exploring coil.

Table I.

The field-strength computed a) from measurements with the exploring coil (H_a), b) from measurements of the susceptibility of the water (H_b).

S (mm)	H_a (Oe)	h (mm)	H_b (Oe)	$H_a - H_b$
116.8	37 880	−0.542	37 820	60
116.5	37 790	.538	37 680	110
116.4	37 750	.537	37 640	110
116.7	37 850	.542	37 820	30
116.6	37 820	.540	37 750	70

We thus obtain the coil areas:

from measurements with the exploring coil . . . . . 1.531 cm²
» » of the susceptibility of the water 1.536 »
Mean value 1.533 cm²

The difference between the two measurements is 4 ‰, which must be considered rather insignificant in view of the great possibilities of error which occur in the determinations.

We made a survey of the fields in conical pole shoes with the pole surface diameters 12, 6, 2 and 0.5 cm. The pole horns for these pole shoes consisted of a FeCo alloy containing 34 % Co. As this alloy has a higher saturation value than soft iron, higher fields can be obtained with it.

In the accompanying figures (5—8) some values are given for the variation of the field strength with the current (I) passing through the magnet. The field rises rapidly at first and afterwards slowly approaches saturation. When the pole shoes were near one another, a considerable remanent magnetism was obtained.

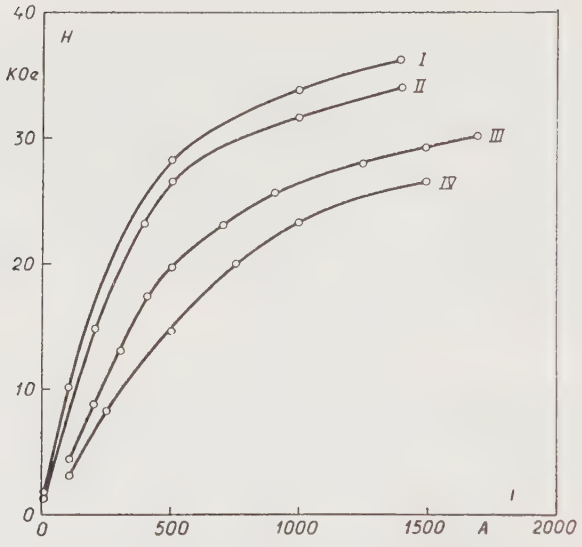

Figure 5. Variation of the Field with Current. Conical Pole Shoes 12 cm Diameter. Air Gap I 3.8 cm, II 4.0 cm, III 8.8 cm, IV 12.1 cm.

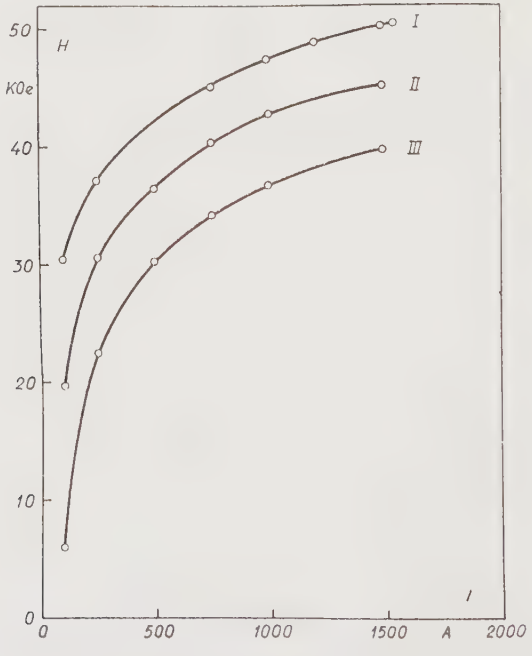

Figure 6. Variation of Field with Current. Conical Pole Shoes 6 cm Diameter. Air Gap I 0.5 cm, II 2.0 cm, III 4.0 cm.

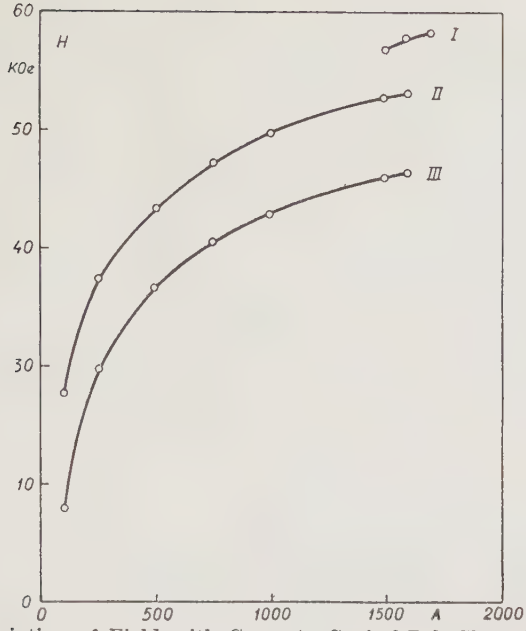

Figure 7. Variation of Field with Current. Conical Pole Shoes 2 cm Diameter. Air Gap I 0.5 cm, II 2.0 cm, III 4.0 cm.

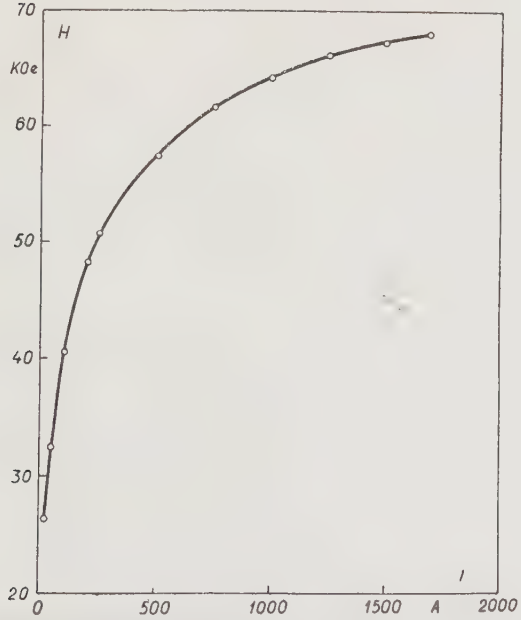

Figure 8. Variation of Field with Current. Conical Pole Shoes 0.5 cm Diameter. Air Gap 0.2 cm.

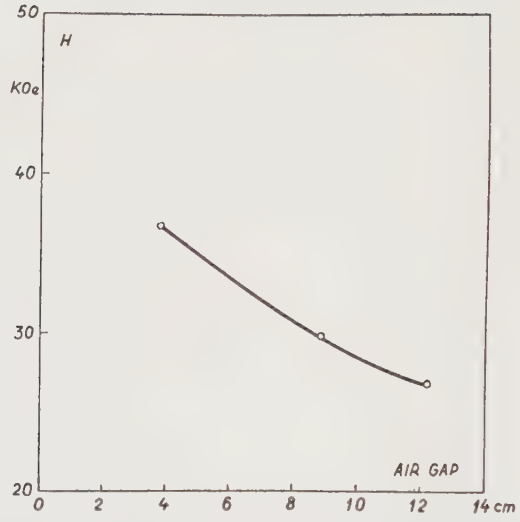

Figure 9. Variation of Field with Air Gap. Conical Pole Shoes: 12 cm Diameter. Current 1 500 amp.

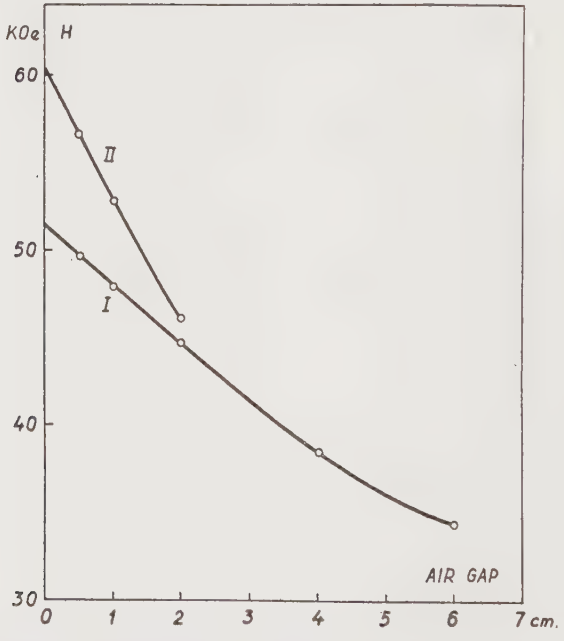

Figure 10. Variation of Field with Air Gap. Conical Pole Shoes I 6.0 cm Diameter. II 2.0 cm Diameter. Current 1 500 amp.

As regards pole surfaces with a diameter of 12, 6 and 2 cm, curves are also given for the variation of the field with the pole distance, when I = 1 500 amp (figures 9—10).

The homogeneity of the field is shown by the following values for pole shoes 12 cm in diameter, when the pole distance is 8.86 cm and I = 1 500 amp (figure 11). To a distance of 5 cm from the centre, the field strength had fallen 4 %. Still more homogeneous fields were also measured. The fields in which the nitro-

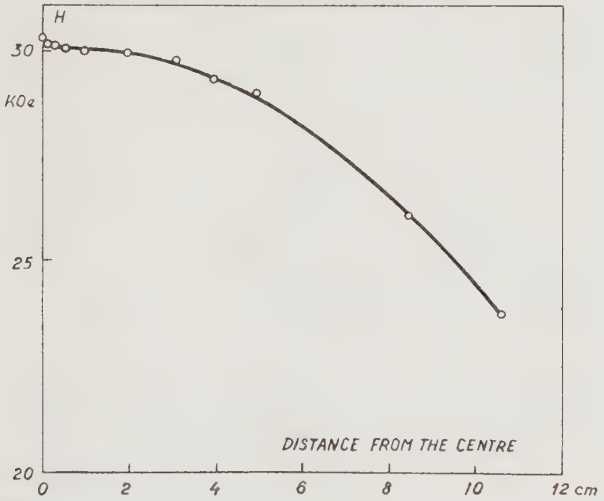

Figure 11. Variation of Field with Distance from Centre. Conical Pole Shoes 12 cm Diameter. Air Gap 8.9 cm. Current 1 500 amp.

benzene's Cotton-Mouton constant was afterwards measured varied for I = 1 700 amp by about 2 % to a distance of 5 cm from the centre.

In measuring the homogeneity, a phenomenon to which Prümm (4) had first drawn attention, is frequently observed. The maximum field is obtained in the centre. The field falls rather rapidly at first and then remains constant for a while before it definitively decreases towards the edge of the pole shoes. Generally this change was not so marked as that recorded by Prümm, being merely 1—2 %, as compared with 3—4 % according to Prümm. This disparity seems to be due to external factors. It is presumably possible with pole shoes constructed as proposed by Du Bois to obtain better values for the homogeneity.

Some interest attaches to the values for the variation of the field with the current strength, as regards pole shoes 0.5 cm in diameter. Here the highest fields were obtained. At 1 700 amp and a pole distance of 0.2 cm, 68 500 Oe (450 000 ampere turns) was obtained. With a minor readjustment of the transformer, it is possible to work with a larger current strength and then attain 70 000 Oe at 2 000 amp.

J. Stefan (5) found that, if the lines of force are concentrated by using conical pole shoes, the maximum was attained when the pole angle was arctg $\sqrt{2} = 54° 44'$. For pole shoes of the kind used by us, Stefan found that the following formula was applicable in measuring the field strength:

$$H = 4\pi I \left(1 + \frac{2}{3\sqrt{2}} \log \frac{r}{a\sqrt{2}} - \frac{1}{\sqrt{3}}\right) = 4\pi I (0.2893 + 0.8863 \log r/a)$$

$2r$ = diameter of pole surface
$2a$ = distance of pole surfaces
I = intensity of magnetization.

This formula is also in conformity with our values.

From a theoretical point of view, Du Bois (6) also made a thorough investigation of the optimal conditions.

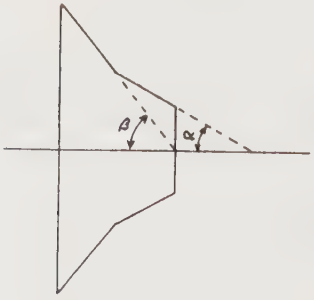

Figure 12.

Du Bois found that more homogeneous fields could be obtained with pole shoes of another character, namely "Kegelstützpole mit vortretenden Stirnflächen". For these pole shoes, under the assumption that $\alpha = 54° 44'$ and $\beta = 79° 26'$, one obtains homogeneous and strong fields (figure 12).

Some values for the fields of wedge-shaped pole shoes are given also in figures 13—14. Such pole shoes are best adapted for computing the transversal double refraction. In this case the pole shoes were made of soft iron. The profile, which is similar to that of Du Bois' conical pole shoes, is shown in figure 12.

Because of the interest for double refraction measurements some curves have been given for the variation of the field with

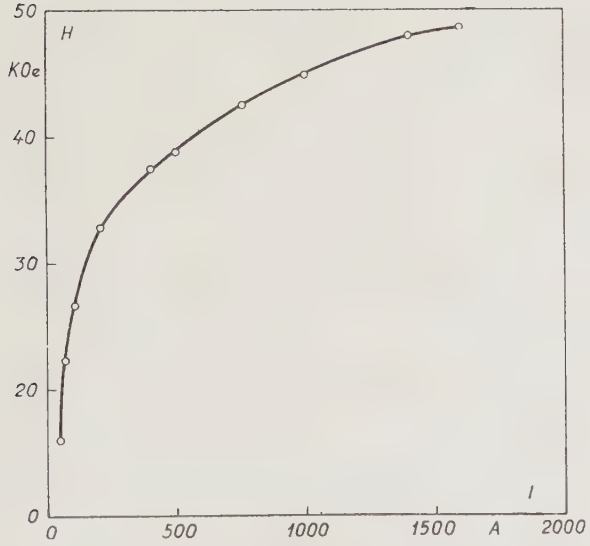

Figure 13. Variation of Field with Current. Pole Shoes: 10×1 cm^2. Air Gap 1 cm.

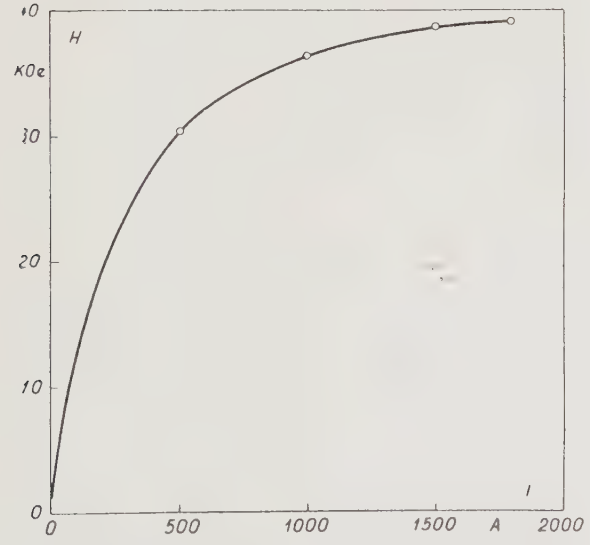

Figure 14. Variation of Field with Current. Pole Shoes: 58×1 cm^2. Air Gap 2 cm.

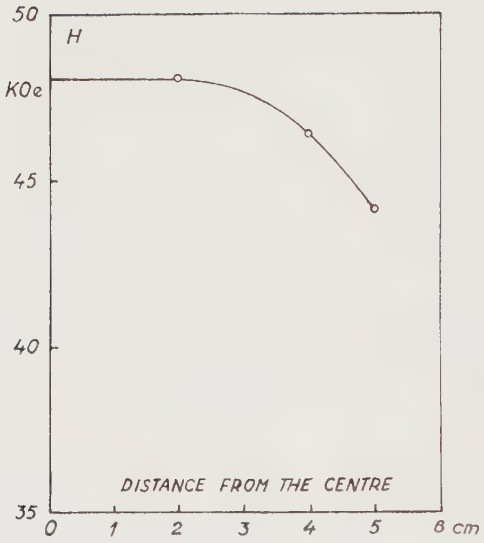

Figure 15. Variation of Field with Distance from Centre. Pole Shoes 10×1 cm^2. Air Gap 1 cm. Current 1 500 amp.

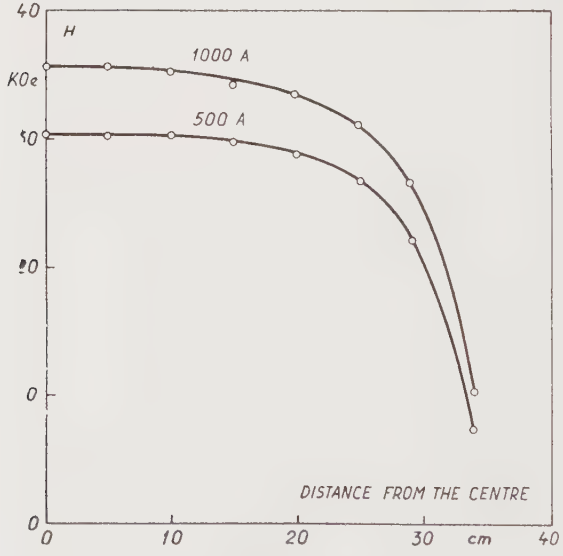

Figure 16. Variation of Field with Distance from Centre. Pole Shoes 58×1 cm^2. Air Gap 2.2 cm. Current 1 000 amp. 500 amp.

the distance from the centre, especially as regards pole shoes 10×1 cm^2 and 58×1 cm^2 (our largest pole shoes of that kind).[1] (Figures 15—16.) For these pole shoes the field in a lateral direction was not quite homogeneous, being about 2 per cent. larger next to the pole surfaces.

As regards pole shoes 58×1 cm^2, a computation was also made of the expression $\int H^2 dl$, which is of interest for the measurement of the Cotton-Mouton constant. This expression, when the measuring tube was 60 cm in length, was 8.3 10^{10}. The effect then used was 110 kwatt. It may be mentioned that the Cotton magnet, with a 63 cm tube, gave the value of $\int H^2 dl = 5.4\ 10^{10}$ with the electromagnet alone and when the effect was 92 kw, and the value of $\int H^2 dl = 10.4\ 10^{10}$ when auxiliary coils with 480 kw were employed. (Cotton and Belling (7).)

Comparison between the Upsala and Bellevue magnets.

Cotton and Dupoy (8) measured the fields for the Bellevue magnet without auxiliary coils. These measurements were made with a maximum effect of 93 kw and 500 000 ampere turns.

At Upsala we measured a large number of fields at 108 kw and 440 000 ampere turns. Though the number of ampere turns was thus considerably lower, the effect was approximately the same.

The following table shows values for measurements made with the same kind of pole shoes.

Table II.

Diam. of pole surface	Pole distance	Field in KOe	
		Bellevue	Upsala
6 cm	0.5 cm	48.6	50.3
	1	47	
	2	44	45.2
	4	39	39.8
2 cm	0.5 cm	56.8	57.9
	1	52.8	52.8
	2	46.4	46
0.5 cm	0.5 cm	60	62.6

[1] We have pole shoes of this type with the following surfaces: 10×1 cm^2, 25×1 cm^2 and 58×1 cm^2.

The values do not show much difference. It should be noted, however, that we have possibilities of obtaining larger effects without any auxiliary coils. The Upsala magnet must therefore be considered somewhat better in this respect than the Bellevue magnet. By the arrangement of auxiliary coils round the pole shoes, still higher fields have indeed been attained, in some cases, with that magnet. This, however, at the expense of an immense consumption of energy. There is nothing to prevent us, if desired, from making similar arrangements at Upsala. But, in view of the expensiveness of the effect required (3 or 4 times as large), the result seems quite out of proportion to the additional cost.

CHAPTER III.

Determination of the Cotton-Mouton effect in some standard liquids.

In 1901 Kerr (9) observed that finely divided Fe_3O_4 particles suspended in water became double refracting when the light passed the medium normally to the field of force. At about the same time, quite independently of Kerr, Majorana (10) discovered the same phenomenon in colloidal solutions of ferric oxide and investigated it more closely. Some years later Cotton and Mouton started intensive work on the study of this phenomenon in colloids. In these investigations, proceeding from analogies with the known electro-optical Kerr effect in dense liquids, they soon found a marked magnetic double refraction in nitrobenzene (1906). (Cotton and Mouton (11).) Not long afterwards they discovered the same effect also in other liquids, especially aromatic hydrocarbons. After the two discoverers, magnetic double refraction in dense liquids is called the Cotton-Mouton effect.

It may be mentioned that this effect was subsequently observed also in gases far away in the spectrum from resonance lines where special circumstances hold.

The path difference (ψ) occurring in magnetic double refraction, as measured in a vacuum wave lengths (λ_0) of the incoming light, is dependent on the field strength (H) in homogeneous fields, expressed in Oerstedt, and on the path of the light in the liquid (l), expressed in cm. It thus varies in accordance with the following relation, empirically found by Cotton and Mouton (12), for a homogeneous field, where the path of the light-ray is normal to the field:

$$\frac{\psi}{\lambda_0} = C_m H^2 l .$$

The constant C_m is called the Cotton-Mouton constant; it is a material constant dependent on the temperature and the vacuum wave-length of the light used, as well as on the nature of the substance.

The above relation is applicable to gases and dense liquids.

This constant has been defined also in other ways.

Szivessy (13), apparently from considerations of convenience, often uses a constant $C_m \lambda_0$.

Debye (14) has introduced a constant $K_m = C_m \frac{\lambda_0}{n_0}$, and König (15) a molecular C_m constant which, as regards diamagnetic substances, has the following formula

$$\bar{C} = \frac{K_m 6 n_0^2}{(n_0^2 + 2)^2} \frac{M}{\varrho},$$

where n_0 is the index of refraction of the medium outside of the magnetic field,

M is the molecular weight of substance,

ϱ is the density of the substance.

These constants, which have been used also for liquids by some investigators, are chiefly of interest for gases, where they have a certain significance according to the Langevin-Born theory. For liquids in regard to which a satisfactory theory is still lacking, it seems advisable to keep to the Cotton-Mouton definition.

For a field which is not perfectly homogeneous, the relation is

$$\frac{\psi}{\lambda_0} = C_m \int_0^l H_\perp^2 \, dl,$$

where $H_\perp$ denotes the component of the magnetic field normal to the light ray.

With the wedged-shaped pole shoes commonly used in computing the Cotton-Mouton effect, the field, as we have seen, is rather unhomogeneous. It is then usual to calibrate with some liquid which has a known C_m. As a rule, nitrobenzene or some liquid having a C_m previously calibrated against nitrobenzene, is taken as a standard.

Nearly all the computations hitherto made — such as those of the American and Indian school, with a compensator of the Forrest-Palmer type — are relative. In this way, however, relative computations for several hundred substances have become available. (See Landolt and Börnstein: Physikalisch-chemische Tabellen or International Critical Tables.)

Absolute determinations, on the other hand, are few in number, being recorded merely in four publications.

The values given in these computations show rather large discrepancies. It was therefore of some interest to attempt to make an absolute determination of the Cotton-Mouton constant, especially as, so far as the author is aware, no attention has been devoted to the degree of purity of the calibration liquids employed.

The magnetic fields adopted.

The magnetic field to be adopted was computed with the method indicated above for the field of strength at which the measurement was to be made.

The field was fairly homogeneous. For the computation of $\int Hdl$ a numerical integration of the length of the experimental tubes was made. The results are summarized in table III.

Table III.

l	500 amp	1 000 amp	1 500 amp
3 cm	$18.65 \cdot 10^8$	$27.26 \cdot 10^8$	$31.56 \cdot 10^8$
9 cm	$54.92 \cdot 10^8$	$81.26 \cdot 10^8$	$93.97 \cdot 10^8$

The double refraction in benzene was computed in the two tubes. The differences between the ratio of the double refractions measured and those calculated were

I	Δ_9/Δ_3	$\int_0^9 H^2 dl \Big/ \int_0^3 H^2 dl$
500	2.94	2.94
1 000	2.96	2.98
1 500	2.97	2.97

As will be seen, the differences lie within the limits of errors in measurement. In most cases the longer tube was afterwards employed.

In order to control the different measurements, the field was then measured in the centre. A correction was made, where required, for any modification in the field strength. The changes in the field were in general quite small.

Optics.

The general design of the apparatus is shown in figure 17. The image of the arch A is projected through the achromatic

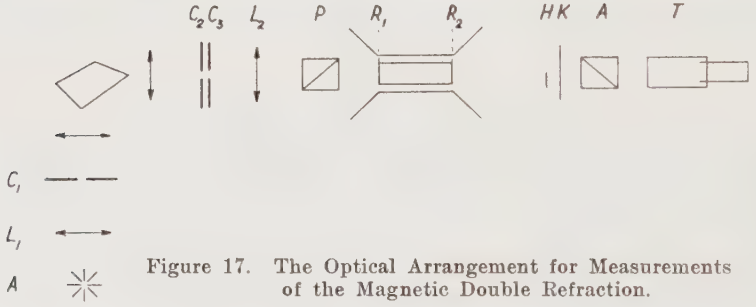

Figure 17. The Optical Arrangement for Measurements of the Magnetic Double Refraction.

condenser L_1 on the slit C_1 of the monochromator. The image of the second slit C_2 is projected by the illumination lens L_2 on the first cell diaphragm R_1. The image of the slit C_3 in front of the monochromator is projected on the half shade diaphragm H. P and A are the two nicols. K is the compensator plate. T is the telescope.

The distances we had in these cases were $L_2—R_1 = 1.5$ metres, $R_1—H = 2$ metres, $f = 33$ cm.

When performing measurements of double refraction much attention must be given to the light source. The sensibility of the arrangement increases with the illumination on the retina. Since by magnetic double refraction we have only small effects the level of illumination is low. The light source must possess an intrinsic brightness as high as possible.

Therefore we used a Philips high-pressure mercury arc lamp, type Sp 500 W, as a source of light. A lamp of this type gives marked, though rather broad mercury lines. In view of the

strong background intensity a monochromatic illuminator must be employed. The author has compared this lamp with a carbon arc lamp having coppered carbons, operated at 42 amp. As standard a tungsten filament lamp operated at 17 amp was used.

The qualitative measurements were carried out in accordance with the three nicols prism method and the densities on a photographic plate were then compared.

It was then found that the green light emitted by the mercury lamp was superior in intensity to that of the carbon arc light now obtainable. In red, on the other hand, the light given by the mercury lamp was of very low intensity. It should be mentioned, however, that no tests have yet been made with the more modern mercury arc lamps in which the red light is intensified by lumniophores.

In a mercury lamp of this type the arc must be placed horizontally. As the arc is rather narrow, certain drawbacks arise as the slit of the monochromatic illuminator is vertical. In this respect the carbon arc lamp is superior. The latter might also be improved by the use of suitable salts for the impregnation of the carbons, so as to obtain a spectrum with prominent lines showing a greater intensity of light. At the present stage the two types of lamp seem to be of approximately equal merit in a certain range of the spectrum. The carbon arc lamp is best adapted for liquids in which the dispersion is small. In the case of marked dispersion on the other hand the mercury lamp is superior because monochromatic light can here more easily be obtained.

The light path was designed in accordance with the principles given by Björnståhl (16) for obtaining a light path free from reflections and so that every point of the half shade in the compensator received light from all parts of the light source in order that it might be evenly illuminated and furthermore so that reflections did not occur. The zero point variation of the compensator does not exceed one or two minutes.

The cells employed in these tests were made of Jena glass without any thermostat. With a view to further tests a cell intended for the wedge-shaped pole shoes was constructed of brass. The tube (10 cm long) was gilt. Arrangements for letting the thermostat-liquid circulate all round the tube and the sides of

the end-glasses were performed. The width of the tube was 7 mm and the outside width was 10 mm. Any tests with this tube have not yet been carried out while, on account of delivery difficulties, the thermostat which we intended to use has not yet been available.

In most of the measurements a Brace compensator was employed. This compensator consists of an extremely thin mica plate, the half shade or the sensitive strip covering half the field of vision and placed at an azimuth of 45° against the crossed prisms. The latter, like the compensator plate, is mounted between two cover glasses, free from double refraction, in Canada balsam. The compensator plate covers the whole field of vision and is fixed in a graduated circle scale.

In these tests the compensator plate was always placed next to the analyzer. The principal sections of the polarizing prisms were crossed, forming an angle of 45° with the lines of force. The telescope was focussed on the sensitive strip.

The compensator was now turned to get a field of view uniformly illuminated. The magnetic current was switched on and the compensator was set for a match again.

The theory of the Brace compensator, after preliminary work by Tuckerman (17) and Chaumont (18), has been more throroughly studied by Bergholm (19), Szivessy (20) and Björnståhl (21).

The plates of the compensator can when measuring accidental double refraction be arranged according to two alternatives: 1) Polarizing prism (P), Double Refraction Medium (D), Sensitive Strip (H), Compensator Plate (K), Analyzing prism (A), or in alternative 2) $P\,D\,K\,H\,A$. We adopted alternative 1). The formula for this alternative, when the magnetic force forms an angle of 45° with the analyzer, is as follows:

$$\operatorname{tg}\left(\Delta + \frac{\Delta_h}{2}\right) = \frac{\sin \Delta_0 \sin 2\psi}{1 - 2 \sin^2 2\psi \sin^2 \frac{\Delta_0}{2}}$$

where Δ is the unknown phase difference,

Δ_0 is the phase difference of the compensator plate,

Δ_h is the phase difference of the sensitive strip,

ψ is the azimuth of the principal plane of the compensator plate relatively to the analyzing prism.

If we have $\Delta = 0$, we obtain

$$\operatorname{tg} \frac{\Delta_h}{2} = \frac{\sin \Delta_0 \sin 2\psi_0}{1 - 2 \sin^2 2\psi_0 \sin^2 \frac{\Delta_0}{2}}$$

where ψ_0 represents in this case the angle between the principal plane of the compensator and the analyzer.

For small values of the angle ψ, we obtain

$$\operatorname{tg} \Delta = \sin \Delta_0 (\sin 2\psi - \sin 2\psi_0).$$

Introducing the rotation of the compensator plate, we obtain $\psi - \psi_0 = \theta$ and the preceding equation can be written:

$$\operatorname{tg} \Delta = 2 \sin \Delta_0 \sin \theta \cos (2\psi_0 \pm \theta).$$

Bergholm has indicated the range in which this approximative formula can be used.

The influence of the apparatus constants on the sensitiveness of the Brace compensator can be computed from the percentage difference in illumination between the two halves of the field of vision, due to the change in the phase difference. If dI/I denotes the percentage difference in illumination and $d\Delta$ a minor change in the phase difference, we obtain the expression

$$dI/I = \frac{4(d\Delta)}{\Delta_h + 2\Delta}.$$

According to this formula, the sensitiveness is greater, the smaller the phase difference is in the sensitive strip. The illumination is determined by the latter. Its phase difference should therefore be as small as is feasible in view of the intensity of the source of light and the individual sensitiveness of the eye. The sensitiveness of the compensator is independent of the phase difference of the compensator plate.

For other reasons, however, Δ_0 must be chosen rather small in order to avoid loss of accuracy in measurement.

The least observable phase difference is shown by the preceding formula to be

$$(d\Delta)_{\min} = \frac{\Delta_h}{4} \frac{dI}{I}.$$

Differences down to one per cent in illumination can be observed, and, if the phase difference in the sensitive strip is $4\ 10^{-3}\ \lambda$, we get $(d\Delta)_{min} = 10^{-5}\ \lambda$, a limit which was actually attained.

The azimuth of the ellipse in the Brace compensator had to be determined by a special test.

If a $\lambda/4$ plate is introduced in the zero azimuth in front of the Brace compensator and afterwards when the double refracting medium is introduced, the $\lambda/4$ plate must then be turned at an angle Ω, in order that the two fields of vision may again have the same illumination. If we write the amplitude ratio $\operatorname{tg} 2\gamma = a_{\parallel}/a_{\perp}$, where $a_{\parallel}$ is the amplitude component parallel to the field and $a_{\perp}$ is the component normal to the field, we have $\operatorname{cotg} 2\gamma = \operatorname{tg} 2\Omega \cos \Delta$. In order to eliminate the error which arises owing to the inexactness of the $\lambda/4$ plate, it was turned at an angle of 90° and the reading was repeated. We then obtain[1] $\operatorname{cotg} 2\gamma = \operatorname{tg} (\Omega_1 + \Omega_2) \cos \Delta$. Or when $a_{\parallel}/a_{\perp} = \varrho$.

$$\frac{1-\varrho^2}{2\varrho} = \operatorname{tg} (\Omega_1 + \Omega_2) \cos \Delta.$$

The phase difference in the mica plate serving as a compensator was determined with a Szivessy half shade compensator, the phase difference of which had previously been computed with a Soleil half shade compensator.

The constants of the mica plate used as a compensator are recorded in Table IV.

Table IV.

λ mμ	Δ_0	$2\psi_0$
438	10° 18′	
492	9° 4′	4°
546	8° 38′	
578	8°	4°

The sign of the phase difference was determined with a sodium glass plate. The phase difference is positive when it coincidences in sign with the glass plate extended in the direction of the field of force.

[1] In Bergholm's work there is evidently a misprint here.

Adjustment of the apparatus.

The measuring cell was filled with carbon tetrachloride and the light path was adjusted so as to eliminate any observable rotation effect of the plane of polarization. The tube was then filled with nitrobenzene and the polarization prisms were adjusted so that no phase difference was observable. The prisms were then turned 45°. Control tests were made which showed, that with carbon tetrachloride no phase difference appeared.

Possible errors.

The maximum error in measurement appears to be due to the difficulty in determining the phase difference of the compensator plate. The margin seems to be about 1 per cent.

As the field strength assumes a quadratic form, any error in this determination will be doubled. If, for example, the error in determination is 3 ‰, the actual error will be 6 ‰.

Other errors, such as faults of alignment, uncertainties in regard to temperature, or errors in monochromatization cannot represent any large figures; taken together, they can scarcely amount to more than one per cent.

On this basis, we have to expect an error of about 2.6 per cent for the calibration liquids here determined.

Definition of Standard Liquids.

The Cotton-Mouton constant was determined for the following substances: nitrobenzene, benzene, toluene, chlorobenzene and acetone. Some attention was devoted to the purification of these liquids.

All who have previously attempted to make absolute determinations have taken "Kahlbaums purissimum" (or some other similar preparation) direct. Some discrepancies in the value may conceivably depend on the use of ill-defined substances.

This is strikingly shown in regard to the nitrobenzene proposed by Cotton and Mouton as the highest standard. According to them, nitrobenzene has the most exactly determined constant of all substances (see also Landolt-Börnstein: Physikalisch-che-

mische Tabellen), although the liquid has merely been defined as a trade preparation.

Nitrobenzene contains a good deal of water, besides which it is evidently a substance of unknown nature. It has long been known that when newly distilled nitrobenzene, which has a very faint yellow colour, is allowed to stand for a time, it darkens considerably.

Hehlgans (22) has made measurements of the conductivity and breakdown voltage of nitrobenzene. It may be of interest here to give an account of his measurements. They are summarized in the following table V.

Table V.

Purification	Spec. resistance ohm/cm	Breakdown voltage volt/cm
Trade preparation	$5 \cdot 10.^7$	$4.8 \cdot 10^4$
Electrochemically purified	$8 \cdot 10.^7$	
Treated with Al.oxid	$8 \cdot 10^9$	$12.9 \cdot 10^4$
Treated with Al.oxid and vacuum distilled	$8 \cdot 10^{10}$	$14.5 \cdot 10^4$

As shown by the results, these properties are considerably modified by the purification.

In investigating the Kerr effect, Hehlgans found that the conductivity was greatest in the middle of the distance between the cell-plates, and that the conductive impurities diminished at the electrodes. According to Hehlgans, it may be inferred from this difference that the impurity is an acid.

That the method of purification is of some importance for the magnetic double refraction, was found by the author in his experiments. It was in fact ascertained that the value of C_m was a function of the time.

Nitrobenzene was purified by washing with distilled, weakly alkaline water and was then dried with calcium chloride. In both processes the liquid was thoroughly shaken. It was then allowed to freeze out, so that the mother-liquor was about 50 per cent of the substance. The nitrobenzene thus frozen out was then subjected to vacuum distillation

Immediately after the vacuum distillation an approximately 10 per cent lower C_m constant was found. It then gradually rose to the same magnitude as the C_m constant of the non-treated substance. In the following table VI are given some values from such an experiment.

Table VI.

Frozen-out and vacuum distilled			Frozen-out		
Temperature	Time (hours)	C_m 10^{13}	Temperature	Time (hours)	C_m 10^{13}
18.2	0	28.1	17.9	0	31.7
18.2	1/2	29.2	17.8	2	31.2
18.2	1	29.7	17.8	3	31.1
18.1	2	30.4	18.2	7	30.85
18.1	3	30.5	18.3	20	30.85
18.1	4	30.55			
18.1	6	30.73			
18.3	24	30.85			
18.1	48	30.85			

On the other hand, nitrobenzene which had merely been frozen out or distilled with aluminium oxide in a column apparatus without a vacuum showed a somewhat higher C_m constant, which, however, gradually fell towards the same C_m value as the non-treated nitrobenzene. A few dispersion measurements were made with regard to the latter. The dispersion $C_{m\,438}/C_{m\,546}$ varied somewhat with the change in C_m (from 1.33 to 1.38). This change seems to lie beyond the limits of error.

For absolute measurements, these results are of some interest. If nitrobenzene is subjected to purification, the age of the calibration liquid must be determined. Frozen-out nitrobenzene should, therefore, not be immediately used for calibration.

It is rather difficult to give a satisfactory explanation of these results. Evidently, however, they have some connection with the fact that nitrobenzene is a highly associated liquid, and that the double refraction is sensitive to variations in the degree of association.

König (15), in using the molecular Cotton-Mouton constant ($\bar{C}$) which he considered to be independent of the state of aggregation, found that, for nitrobenzene $\bar{C}_{\text{gas}} < \bar{C}_{\text{fluid}}$. $\bar{C}_{\text{gas}}$ was extremely small. Only the upper limit was attained. For the Kerr effect

the corresponding constants in nitrobenzene are $K_{gas} > K_{fluid}$. A similar result might be expected also with regard to the magnetic effect. This is in fact the case as regards benzene. That this does not apply to nitrobenzene is evidently due to the fact that the liquid is so readily associable, and that thereby its magnetic anisotropy alters.

It may be presumed that the values given here do not apply to nitrobenzene when completely free from water and reaction products. White (24), in his purification tests, found that even the most thoroughly purified nitrobenzene showed cataphoresis effects when an electrostatic field was applied across the measuring cell.

From our experiments we may conclude that for nitrobenzene it takes some time before a statistical equilibrium is reached. It is possible to compare the process with a chemical reaction. The molecules must have a certain activation energy before the association will take place.

That the effects are so clearly shown by nitrobenzene and not by the other liquids depends on the very strong directing forces when nitrobenzene associates.

The cases where at the beginning the double refraction is higher we refer to impurities. Through the treatment other equilibria will build up in the liquid and the association of the impurities with the nitrobenzene molecules will give quite different values of the double refraction. Even here one can expect that it ought to take time before equilibrium is reached.

It is possible that Wolfke and Mazur (23) had such anomalies when they found a transition point for nitrobenzene at 9.6° C. A point which no other investigators since that have detected.

Some effects of the purification was observed also in regard to chlorobenzene. The difference here, however, was considerably smaller. The dried and newly distilled chlorobenzene showed a value about one per cent lower then that of the aged substance.

The author had previously investigated the conductivity of chlorobenzene. It changes on purification from 10^{-9} to 10^{-12} ohm^{-1} cm^{-1}.

Changes resulting from purification were observed also in acetone. Purified acetone showed a 10 per cent higher value than

acetone taken straight from a bottel. This substance too contains many impurities, and changes according to the degree of purity had therefore been expected.

The liquids were purified in the following manner:—

Benzene: "Kahlbaum's analysenrein" (thiophen-free), was distilled in a column apparatus.

Toluene: ("Kahlbaum's") was distilled in a column apparatus.

Chlorobenzene: ("Kahlbaum's purissimum") was washed first with 1-n Na_2CO_3 and then several times with water; it was then dried with P_2O_5 and distilled in a column apparatus.

Nitrobenzene: was first washed with distilled alkaline water and then dried with calcium chloride and afterwards boiled with aluminium oxide and distilled at low pressure in a column apparatus. The nitrobenzene was aged for three days.

Acetone: which contains many impurities, was treated more thoroughly. Kahlbaum's acetone was allowed to stand for three or four days with potassium permanganate, and was then boiled under reflux for two hours with that substance. The acetone was then distilled off and dried over water-free potassium carbonate and re-distilled before use.

Measurements.

The results of measurements at $\lambda_0 = 546$ mμ are given in table VII. In view of the high intensity of the light and the great sensibility of the eye, the compensator with a suitable half shade in these tests gave there the maximum sensitivity. The values found by different investigators in their absolute determinations (extrapolated to the same wave-length on the basis of the dispersion curves) are given in the following columns.

As the author's values were measured at a temperature of about 1—2 degrees below those of the other investigators, it might be expected that the former values would be somewhat higher.

Cotton-Mouton's values and those of König, however, are considerably lower than all the others. The disparity is evidently due to some systematic discrepancy in the determination of the fields. Unduly low values may be obtained if the field is not homogeneous and has been measured only in the centre. This may be the case as regards König.

Table VII.

Substance	Investigator									
	Snellman		Matull (25)		Szivessy (26)		Cotton and Mouton (27)		König (28)	
	$C_m 10^{13}$	temp.	$C_m 10^{13}$	temp.	$C_m 10^{13}$	temp.	$C_m 10^{13}$	temp.	$C_m 10^{13}$	temp.
Benzene	7.12	18°	6.80	20°			6.24	18°.3		
Toluene	7.30	18°.5	7.28	20°	7.30	19°.4	6.47	17°.5		
Chlorobenzene	8.88	18°.5			8.90	19°.8	7.50	20°		
Nitrobenzene	30.9	18°.3			27.0	19°.8	26.6	20°	25.4	20°
Acetone	0.49[1]	18°.8					0.44[1]	20°		

When using large magnets there is also the risk that stray fields may interfere with the measurement of the field strength.

For nitrobenzene Szivessy, curiously enough, has obtained a value corresponding to that of Cotton and Mouton, although it was determined in the same experimental series as the values for toluene and chlorobenzene. Szivessy himself makes no comment on this remarkable discrepancy.

The relative values (b), when the C_m constant of nitrobenzene is put equal to 100, agree, within the limits of error, between the author's values and those of Cotton and Mouton for the yellow line 578 mμ as shown in table VIII.

The greatest difference is shown by acetone. The author, however, found that as regards non-treated acetone a value $b = 1.58$, which closely corresponds to that of Cotton and Mouton, was obtained. Acetone is often contaminated with methyl alcohol, which lowers the value.

These tests show that benzene and toluene are the substances best adapted as calibration liquids. From many points of view, nitrobenzene is not a happy choice. It is not correct to take such a non-definable liquid as the highest standard, and it is scarcely desirable to select a liquid in which the Cotton-Mouton con-

[1] For this values the wave-length is 578 mμ.

Table VIII.

Substance	Investigator	
	Snellman	Cotton and Mouton
	b	b
Benzene	23.1	23.3
Toluene	24.1	24.5
Chlorobenzene	28.7	28.8
Acetone	1.68	1.60

stant differs so widely from that of most of the aromatic hydrocarbons.

It is easier to give a chemical and physical definition of benzene and toluene. As regards these substances, however, extensive measurements of the dependence on temperature are still lacking.

Matull's and the author's values for benzene lie within 2 per cent, whilst their values, as well as those of Szivessy, for toluene do not differ even as much as one per cent.

These agreements are well within the limits of error and must be considered satisfactory for a constant in the determination of which the possibilities of error are so great.

Dispersion.

The dispersion was at the same time investigated within a smaller part of the spectrum.

With the aid of the Cotton-Mouton constants reckoned at different wave-lengths of light, the so-called Havelock constant was also computed. As regards diamagnetic substances in a part of the spectrum where the absorption of light is insignificant, this constant may be defined according to the following formula

$$h = \frac{C_m n_0 \lambda_0}{(n_0^2 - 1)^2}$$

n_0 is the index of refraction for the liquid (outside the magnetic field),

λ_0 the wave-length of the light in a vacuum,

h the Havelock constant.

The Havelock constant is considered to be quite independent of the wave-length of light.

The C_m values for different wave-lengths are given in table IX and for the computed h-values. The values of n_0 are taken from Landolt-Börnstein: Physikalisch-chemische Tabellen.

Table IX.

Substance	λ_0 mμ	n_0	$C_m \cdot 10^{13}$	$h \cdot 10^{17}$
Benzene	578	1.5023	6.64	3.65
	546	1.5055	7.12	3.65
	492	1.5126	8.16	3.66
	438	1.5230	10.00	3.83
Toluene	578	1.4975	6.93	3.89
	546	1.5004	7.30	3.82
	492	1.5071	8.30	3.81
	438	1.5168	9.80	4.05
Chlorobenzene	578	1.5282	8.27	4.13
	546	1.5316	8.88	4.13
	492	1.5392	10.08	4.12
	438	1.5500	11.47	4.03
Nitrobenzene (aged)	578	1.5550	28.8	12.92
	546	1.5620	30.85	12.90
	492	1.5740	36.3	12.83
	438	1.5879	42.7	12.85
Acetone	578	1.3592	0.485	0.55
	546	1.3606	0.540	0.55
	492	1.3632	0.630	0.57
	438	1.3671	0.640	0.51

A slight deviation in the values is noticeable. Szivessy, however, did not observe any deviation in his values, which is due to the fact that he did not measure so far out into the violet light. In violet and ultraviolet we may in fact expect a deviation in the values of h, as Havelock's law applies only when the optical anisotropy is small and when we are far from the parts of the spectrum where the liquid has absorption bands.

CHAPTER IV.

The double refraction in some hydrotropic solutions.

Hydrotropy, as defined by Neuberg (29), is the capacity of concentrated aqueous solutions of certain, mainly organic, salts to increase considerably the solubility of many substances sparingly soluble in water.

As examples of salts which act hydrotropically the following may be mentioned: aromatic carbonic acids, sulphonic acids, and the secondary aromatic esters of phosphoric acids. The organic hydrotropic salts are surface-active. Their capacity for dissolving substances ("substrates") is not only confined to a number of simple organic compounds, such as amyl alcohol, ethyl acetate, aniline, nitrobenzene, phtalic acid, etc.; they also act hydrotropically in relation to a number of high-molecular products such as proteins and dyes.

As regards the explanation of this property in the hydrotropic salts, there has been a divergence of opinion.

Freundlich (30), in a study of hydrotropy and Traube's rule, first held the view that a part of this substrate was colloidally dissolved. Subsequently, however, having made diffusion tests with benzoic acid hydrotropically dissolved in aromatic sulphonic acids, Freundlich (31) found diffusion constants which were as great as, or lower than, those obtained for solutions where hydrotropy did not occur. Benzoic acid, however, showed certain anomalies. The diffusion constant was not entirely the same in all layers.

From these tests Freundlich concluded that we were concerned with real solutions and that hydrotropically acting substances, having a great affinity both for water and for organic solvents, possessed the capacity for forming, in aqueous solutions, "solution molecules", capable of dissolving organic molecules.

Neuberg represents the view that the capacity of hydrotropy for increasing solubility is primarily due to the formation of molecular compounds.

Kuthy (32) holds the opinion that we cannot regard a hydrotropically dissolved substance as a real solution or a colloid solution. He thinks that we have all transitions between the two stages for one and the same substance.

The optical activity in a number of such solutions has been studied by Neuberg, Weinmann (33) and Forssman (34).

Neuberg found great variations in the optical activity. His technic enabled him to show that they were due to the hydrotropic dissolution. Forssman found a change in the optical activity in one case, though not in another. In none of these cases, however, had the authors investigated whether such variations might not be dependent on the concentration: the determinations were made merely with a concentration of the substrate.

Pauli and Weiss (35) found changes in the properties of proteins dissolved in hydrotropic solutions.

It seemed therefore to be of interest to ascertain whether further knowledge regarding the hydrotropic dissolution could be obtained from magneto-optic determinations.

Measurements.

As hydrotropic solvents, sodium benzoat (in the sequel termed NaB) and sodium salicylat (in the sequel termed NaS) were employed. Unless otherwise stated, the concentrations were: 60 g NaS or 40 g NaB to 100 g water.

Tests were made on these solutions to see whether the birefringence showed any change not foreseen according to the concentration.

The dependence of concentration was found to be a linear function.

The measurements here as in all the following cases were performed at $\lambda_0 = 546$ mμ and at room temperature (18° C).

The relation between the hydrotropic solvent and the substrate in regard to concentration may be expressed in the partial volumes of one component. If V_1 and V_2 are the volumes of the

two fluids mixed, V will be the volume of the mixture: hence the partial volume of component 1 is $v_1 = \frac{V_1}{V}$. Assuming that the change in volume is smaller than other errors, we put $V = V_1 + V_2$.

The determinations are expressed relatively to the strongest doubly refracting substance, the birefringence of which is put equal to one.

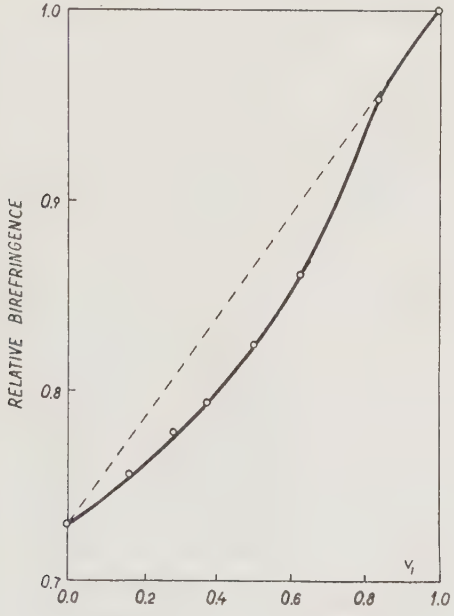

Figure 18. Aniline – NaS.

As a substrate, aniline, which is very slightly soluble in water, was employed. In our measurements, readings on the circle scale were $\theta = 9'$ for saturated aniline solution in water and $\theta = 397'$ for the NaS solution. No correction has been made for the water-solubility of aniline. With the NaS-solution, aniline can be mixed in all proportions, with NaB it is only partly soluble. The curve for aniline in NaS at different volume fractions is shown in figure 18 and table X a. As will be seen from the figure, it is very unsymmetrical. The most marked deviation from an additive course is shown by the solutions containing minor amounts of aniline. A similar shape of curve was shown

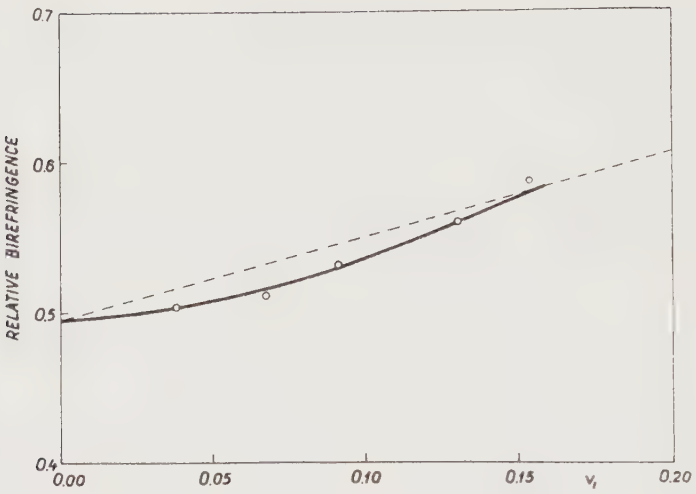

Figure 19. Aniline – NaB.

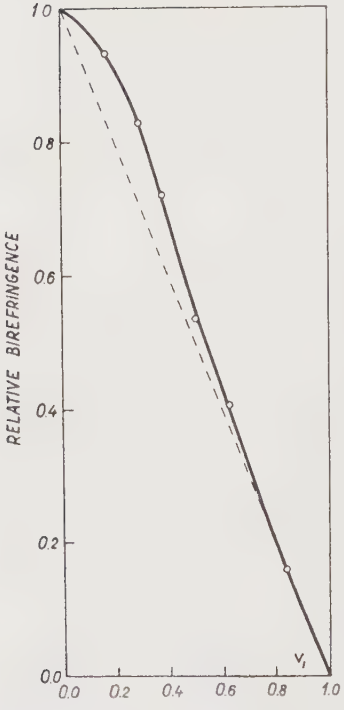

Figure 20. Ethyl Acetate – NaS

by the solutions examined with NaB as a hydrotropic substance as far as the aniline was dissolved. (Figure 19. Table X b.)

Aniline mixtures were also investigated with solutions of 45 g NaS to 100 g water. So far as the aniline was soluble, these solutions gave the same type of curves for the relative double refraction and the volume fraction as in the previous case.

Ethyl acetate, which does not itself show any double refraction measurable in these tests, was dissolved by the two hydrotropic solvents. In NaS it is miscible in all proportions, in NaB merely up to a certain, rather low limit. In both cases we found that, on the addition of minor amounts of ethyl acetate, the double refraction showed no

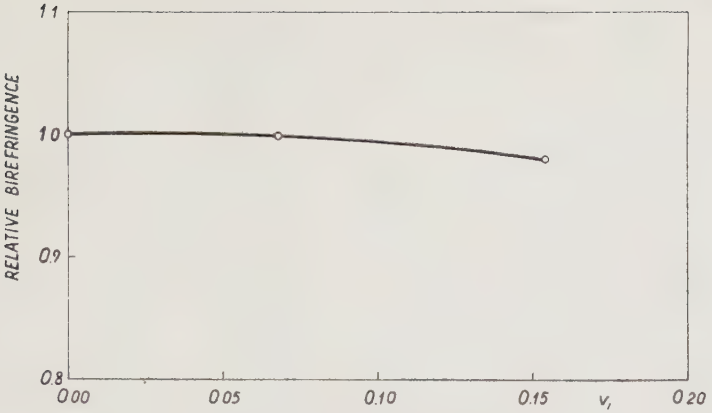

Figure 21. Ethyl Acetate – NaB.

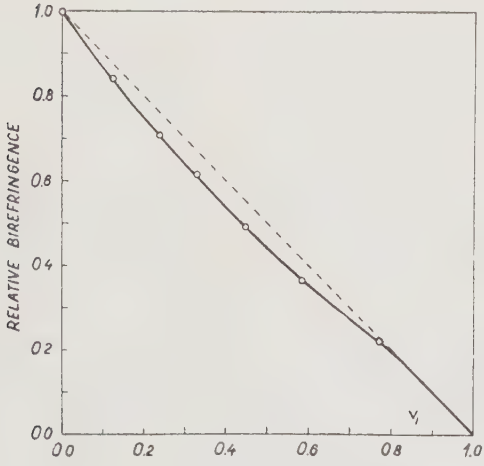

Figure 22. Amyl Alcohol – NaS.

appreciable change, but was reduced at a somewhat stronger concentration; and thus the anisotropy was more marked than might have been expected from an additative behaviour. (Figures 20, 21. Table X c, d.)

Butyl alcohol and amyl alcohol in NaB behaved similarly as the ethyl acetate. In the solutions which contained little of the substrate the anisotropy was greater than expected, in the concentrated solutions it approached the expected addition values.

With NaS as hydrotropic salt we obtained values where the

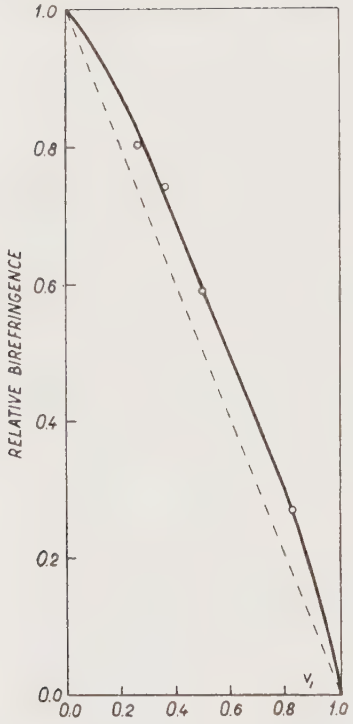

Figure 23. Butyl Alcohol – NaB.

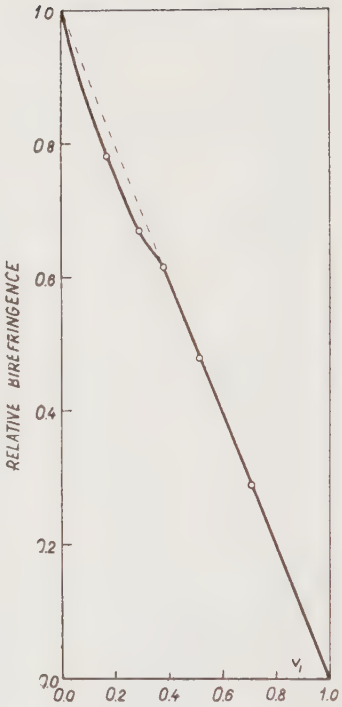

Figure 24. Butyl Alcohol – NaS.

anisotropy was under the expected values in the solutions which had not so much butyl or amyl alcohol. The difference here between solutions of NaS and NaB may depend on structural differences between NaS and NaB. No deviation from the linear course could be observed when varying amounts of acetone were added to NaB. (Figures 22, 23, 24. Table X e, f.)

Discussion.

Magnetic double refraction in mixtures has been studied by several investigators, most thoroughly by Szivessy and Richartz (36) and by Chinchalkar (37). But no satisfactory theoretical discussion of such determinations seems as yet to have been published.

The experimental values are usually compared with those given by the theory of gases.

Table X.

Temp. = 18° C. $\lambda_0 = 546$ mμ.

Table a.

Aniline + NaS.

v_1	Δ'	Relat. Δ
0	117.6	0.729
0.167	121.5	0.754
0.286	125.5	0.778
0.375	127.7	0.792
0.475	129	0.800
0.500	133	0.824
0.624	138.6	0.860
0.833	154	0.954
1	161.3	1

Table b.

Aniline + NaB.

v_1	Δ'	Relat. Δ
0	79.6	0.495
0.0385	81.1	0.502
0.0683	82	0.508
0.0909	85.8	0.532
0.131	90.5	0.561
0.153	95.6	0.592
1	161.3	1

Table c.

Ethyl acetate + NaS.

v_1	Δ'	Relat. Δ
0	114.1	1
0.286	87	0.761
0.375	85.2	0.746
0.833	30.3	0.265
1	0	0

Table d.

Ethyl acetate + NaB.

v_1	Δ'	Relat. Δ
0	79.6	1
0.0682	80.1	1.005
0.0909	82.5	1.035
0.153	77.1	0.968

Table e.

Butyl alcohol + NaS.

v_1	Δ'	Relat. Δ
0	114.1	1
0.167	89	0.780
0.286	76.5	0.670
0.375	69.5	0.609
0.500	54.4	0.477

Table f.

Butyl alcohol + NaB.

v_1	Δ'	Relat. Δ
0	79.6	1
0.161	73.7	0.927
0.286	65.6	0.824
0.375	55.8	0.702
0.500	42.5	0.534
0.624	32.1	0.403
0.833	12.5	0.157

The Lorentz-Lorenz dispersion formula, for a mixture of two components, is:

$$\frac{n^2-1}{n^2+2} = \frac{4\pi}{3}(N_1' a_1 + N_2' a_2)$$

n is the refractive index of the solution,
N_1' the number of molecules of the one kind in the volume unit,
N_2' » » » » » » other » » » » » » ,
a_i the medium polarization of the respective kinds of molecules.

This polarity may be conceived to have resulted from an anisotropically bound electron.

The magnetic field causes a double refraction in the medium. If a Cartesian system of coordinates is introduced, and if the light is conceived to travel in the z direction, we have, for the electric light vector parallel to the x and y axis:

$$\frac{n_x^2 - 1}{n_x^2 + 2} = \frac{4\pi}{3}(N_1' a_{1x} + N_2' a_{2x}); \quad \frac{n_y^2 - 1}{n_y^2 + 2} = \frac{4\pi}{3}(N_1' a_{1y} + N_2' a_{2y})$$

where a_{ix} and a_{iy} denote the mean polarization along the electric light vector parallel to the x or y axis for the different substances; a_{ix} and a_{iy} are now functions of the orientation and the polarization of the molecular axes. The molecules are assumed to be rotation ellipsoids.

The resulting Cotton-Mouton constant, in accordance with the rule of superposition for the constants of the molecules in the mixture, will then be found to be:

$$\frac{n C_m}{(n^2 + 2)^2} = \frac{n_1 (C_m)_1 v_1}{(n_1^2 + 2)^2} + \frac{n_2 (C_m)_2 v_2}{(n_2^2 + 2)^2}$$

where v_1 and v_2 are the respective partial volumes of the two kinds of substances. No change in volume is assumed. Experience has shown that this law is seldom applicable to liquids.

The question as to where the error lies can be discussed from many different angles. To begin with, it may be pointed out that the Lorentz-Lorenz dispersion formula as regards liquids is a mere hypothesis: it has been verified only in the case of gases. For liquids other laws can be formulated.

From various points of view, however, the complete rejection of this theory, in discussing the problem of double refraction, seems scarcely desirable. In determining the molecular polarization, it is in fact customary to discuss how the polarization term itself may be modified by the action of different agencies.

In this connection it should be emphasized that the constant C_m involves the magneto-optical anisotropic term. Thus we do

not know whether it is the optical polarization ellipsoid or the magnetic susceptibility ellipsoid, or both, that is modified on dilution.

For a quantitative discussion of these extremely difficult questions, the material available in the literature seems to be insufficient. Further experiments should therefore be made in different directions. It seems particularly necessary to make thorough investigations of the dependence of temperature.

In substances where the dipole moment is not very active, a semiempirical formula given by van Arkel may be used for the molecular polarization in solutions. In certain cases, it can apparently be used also for the Cotton-Mouton effect. Such formulas yield results indicative of symmetrical deviations for mixed curves.

There is, however, a whole group of substances, including ethyl alcohol, ether and water, to which this formula is not applicable. These substances, in solutions, show a quite different type of molecular polarization, due to the strong associative forces.

Determinations made by Freundlich and Krüger have shown that there can be no question here of micellar formation of the same character as in soft soaps. If there is any aggregation at all, it will be of a much looser nature.

Our results are in good agreement with an explanation of the hydrotropic properties, to the effect that the uncharged part of the organic ion, which is the bearer of those properties, and the substrate, gives, by non-specific van der Waal forces, molecular combinations which are not defined. The solvation of the dissolved substance with the organic part of the hydrotropic salt gives rise to conditions which, from a magneto-optical point of view, completely change the nature of the liquid. Double refraction phenomena are in fact very liable to be affected by changes in the composition of the liquid. It can thus be stated that the deviations which we have found can be explained only on the basis of some association phenomenon. As the physical constants are completely changed by such association, it is very difficult to arrive at quantitative solutions of such problems.

Our experience of different kinds of association effects is also rather insignificant. A long series of experiments is required before these problems can be approached with success.

Whereas in dissolutions of butyl alcohol or ethyl acetate in NaB solution the optical anisotropy is greater than estimated, in aniline it is smaller.

According to determinations made by Chinchalkar, aniline, on dilution with acetone, benzene, carbon tetrachloride and certain other liquids, shows a greater anisotropy than expected. Chinchalkar interpreted his results to signify that the aniline molecules in an associated state showed in the non-diluted solution less anisotropy than that of the free aniline molecules in the diluted solutions.

In aniline the electrical moment is at right angles to the axis of the maximum optical polarization. Aniline thus gives a negative Kerr effect.

The magnetic anisotropy of the susceptibility is such that the molecule adjusts itself with its axis for the maximum optical polarization along the magnetic field. We thus have a positive magnetic double refraction.

It may be presumed that the moment of the aniline molecule somehow contribute to the result that the magnetic anisotropy in the hydrotropic solutions is so totally different from that observed in ordinary solutions.

In order to ascertain whether the molecules of water, which themselves are dipoles, might contribute, in somewhat greater degree, to this result, an experiment was made with a mixture of 8 parts acetone to 3 parts water, in which varying amounts of aniline had been dissolved. This mixture, in the lower concentrations of aniline, gave normal results of the same nature as can be reckoned from Chinchalkar's values for magneto-optical anisotropy. The anisotropy was 1.33 C_{aniline}, calculated on the basis of the whole liquid as aniline.

Sufficient material for enabling us to explain how the forces act in this association is not yet available.

As regards hydrotropic solvents and ethyl acetate or butyl alcohol, there is evidently a marked interplay between the different components in the dilute solution. In such cases it is only the hydrotropic substance which produces any appreciable double refraction effect. The double refraction both of water and the substrate is so slight, that it may be entirely ignored.

Neuberg, in studying the optical activity of amyl alcohol, sug-

gested that a formation of ortho-hydrates possibly occurred, which would be decomposed on increasing dilution. This, however, conflicts with our own observations.

That the effect is greatest in the less concentrated solutions must be attributed to the fact that the affinity of the substrate to the hydrotropic substance is most marked in such solutions, and that additional compounds of some kind have been produced. The latter will naturally show an anisotropy differing from that of the free hydrotropic substance. In the more concentrated solutions, where the hydrotropic properties of the substrate are of less importance, this kind of association does not occur at all or, at any rate, is much less marked, and more normal curves are recorded.

All our experiments along these lines thus point to an interplay between the different components. Molecular additions are formed between the hydrotropic substance and the substrate. Reliable conclusions cannot be drawn in regard to the stability of these complexes. For, as we are concerned here with statistical mean values for the orientation, it is of no consequence whether the clusters are liable to be broken up. Such solutions as those studied here evidently represent a transition to the purely micelle-forming types found in the more markedly hydrophobe-hydrophil soft soaps, which are able, in the micelles, to dissolve substances insoluble in water.

CHAPTER V.

The magnetic double refraction in some dye-stuff sols.

The first investigator who attempted to show a connection between double refraction and dicroism was Babinet. Whereas double refraction relates to differences in the refractive index in certain main directions, the dichroism, or the amplitude effect. relates to a reduction of the amplitude in the same directions. In the case of crystal double refraction Babinet formulated the following rule for these phenomena: the most refracted ray is most intensely absorbed. Majorana (38) in 1902 formulated the same rule for accidental double refraction.

In course of time, however, it was discovered that this rule was not always valid. Zocher (39, 40), who studied the optical anisotropy of dyes, found that Babinet's rule was not invariably applicable to light of a higher frequency, and was able to give a qualitative explanation.

In 1870 Christiansen had discovered anomalous dispersion in the refractive index of intensely coloured solutions. Kundt and others made thorough experimental studies of this matter, and Kettler Helmholtz gave a theoretical interpretation of the phenomenon.

In anomalous dispersion, the index of refraction in an absorption band is changed in the manner shown in figure 25 curve b. The absorption index changes as indicated by c.

Zocher now pointed out that if, for one of the refractive indicies the dispersion is normal, whilst the other refractive index shows an anomalous dispersion, the double refraction will change signs when the absorption is at its maximum (Zocher's rule). In this way, he considered, the deviations from Babinet's rule could be explained.

It is possible, however, to give a more quantitative formulation of the problem.

We shall now calculate the double refraction in a colloidal solution, it being supposed that the rigid particles are embedded in an isotropic homogeneous medium. We assume that a particle has the form of a rotation ellipsoid with the optical and magnetic axis in the same directions as with those of the ellipsoid.

In close connection with the axes of the ellipsoid, we now introduce a system of coordinates (1, 2, 3) and then a space

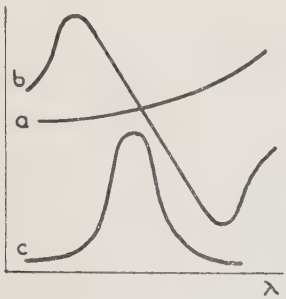

Figure 25. Variation of Refractive Index with Wave-length. a) Normal Dispersion. b) Anormal Dispersion. Variation of Absorption Coefficient with Wave-length. c) Absorption Curve by Anormal Dispersion.

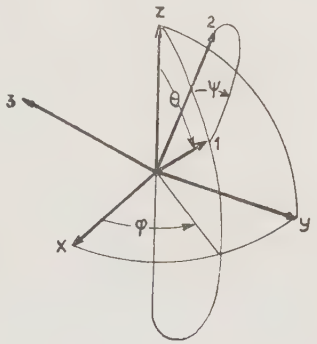

Figure 26. The Situation of the Molecule Fixed Coordinates (1, 2, 3) and the Space Fixed System (x, y, z). The Angles of Euler θ, ψ, φ.

fixed system (x, y, z). The z-axis lies in the direction of the field, and the light-ray passes along the y-axis. The relative positions of the two systems of coordinates are indicated in the usual way by Euler's angles (θ, φ, ψ).

The rotation ellipsoid has the permeabilities μ_1 and μ_2 and the volume v. The potential energy in the field can be written

$$w = -\frac{1}{2}\{g_2 + (g_1 - g_2)\cos^2(1, z)\}\, v H^2$$

with

$$g_1 = \frac{\mu_1 - \mu_0}{4\pi + \frac{\mu_1 - \mu_0}{\mu_0} P_1}; \quad g_2 = \frac{\mu_2 - \mu_0}{4\pi + \frac{\mu_2 - \mu_0}{\mu_0} P_1'};$$

where μ_0 is the permeability of the solvent, whilst P_1 and P_1' are two form factors connected with the eccentricity of e_1 the rotation ellipsoid according to the formula:

$$P_1 = 4\pi \frac{(1-e_1^2)}{e_1^2} \left\{ \frac{1}{2e_1} \ln \frac{1+e_1}{1-e_1} - 1 \right\} \text{ for prolate ellipsoids}$$

$$P_1 = \frac{4\pi}{e_1^2} \left\{ 1 - \frac{\sqrt{1-e_1^2}}{e_1} \text{ arc sin } e_1 \right\} \text{ for oblate ellipsoids}$$

$$P_1 + 2P_1' = 4\pi.$$

For the expression $g_1 - g_2$ we obtain

$$g_1 - g_2 = \frac{4\pi(\mu_1 - \mu_2) - \frac{(\mu_1 - \mu_0)(\mu_2 - \mu_0)}{\mu_0}(P_1 - P_1')}{\left(4\pi + \frac{\mu_1 - \mu_0}{\mu_0} P_1\right)\left(4\pi + \frac{\mu_2 - \mu_0}{\mu_0} P_1'\right)}.$$

Setting aside ferromagnetic substances, where a theoretic treatment is difficult also from other points of view, we have $\mu_i = 1 + 4\pi k_i$, where k_i is the susceptibility. This is now quite a small quantity ($k_i \sim 10^{-6}$). The square of k_i can therefore almost always be neglected. One can then write

$$g_1 - g_2 = (k_1 - k_2).$$

In magnetically isotrope particles where $k_1 - k_2 = 0$, the second term is so small that some orientation owing to the induced moment may be expected only in the case of extremely large particles.

The distribution of the number of particles can now be easily computed on the basis of the Boltzmann distribution law. The number of particles in the volume unit the axes of which as a time mean value lie within a solid angle $d\Omega$ with the limits θ and $\theta + d\theta$, φ and $\varphi + d\varphi$, ψ and $\psi + d\psi$ is

$$dN = Ce^{-\frac{w}{k'T}} \sin\theta \, d\theta \, d\varphi \, d\psi = N' F \, d\Omega$$

k' is Boltzmann's constant,
F the distribution function normalized on one particle,
C the constant obtained from the normalization,
$d\Omega = \sin\theta \, d\theta \, d\varphi \, d\psi$.

C/N' is by the normalization determined through

$$\int F\, d\Omega = 1.$$

The equation of distribution will thus be

$$F = \frac{1}{4\pi}\left\{1 + \frac{v H^2}{2 k' T}(k_1 - k_2)\left(\cos^2\theta - \frac{1}{3}\right) \ldots .\right\}.^1$$

The Lorentz-Lorenz dispersion formula cannot be used for expressing the relation of the colloidal solution to the linearly polarized monochromatic light ray which entered on the double refracting medium.

The Lorentz-Lorenz dispersion formula was originally derived for spherical particles. Since then, however, Faxén (41) has shown that it retains its validity also for any molecular shape whatever, provided that the molecule contains merely a single isotropic resonator. This simple formula is thus not applicable to colloidal particles, which have several connected resonators. In such cases therefore a considerably more complicated formula would be required. As a limiting value where there are a considerable number of resonators, we may regard the particles as consisting of a material with the main dielectric constants ε and ε' and have the form of a rotation ellipsoid with the eccentricity e.

For a system of particles in a vacuum the following formula is applicable:

$$\frac{\nu^2 - 1}{\nu^2 + 2} = \frac{4\pi}{3} N' \alpha$$

where α is the mean polarizability, N' the number of particles per cm^3 and ν the complex refractive index.

If the particles are rotation ellipsoids, the polarizability will depend on the angle between the ellipsoid axis and the electric light vector. If the latter is parallel to the ellipsoid axis, we obtain, under the assumption that the field in the particle can

---

[1] Or generally $$F = \frac{1}{2\pi} \cdot \frac{e^{\frac{v H^2}{2 k' T}(k_1 - k_2)\cos^2\theta}}{\int_{-1}^{+1} e^{\frac{v H^2}{2 k' T}(k_1 - k_2)\cos^2\theta}\, d(\cos\theta)}$$

be regarded as quasi-static for the polarizability in a vacuum (R. Gans (42))

$$\alpha = \frac{v(\varepsilon - 1)}{4\pi + (\varepsilon - 1)P} \quad \text{or} \quad \frac{3}{4\pi}\frac{(\nu^2 - 1)}{(\nu^2 + 2)} = \frac{N' v(\varepsilon - 1)}{4\pi + (\varepsilon - 1)P};$$

where v is the volume of the particle, and P a function of the optical eccentricity (e). The expression for P is just the same as for P_1 on page 54, only $e_1 = e$.

If now the particle is in a medium with the dielectric constant $\varepsilon_0 = n_0^2$, we obtain

$$\frac{n_0^2(\nu^2 - n_0^2)}{\nu^2 + 2n_0^2} = \frac{4\pi}{3} \cdot \frac{N' v(\varepsilon - \varepsilon_0)}{4\pi + \frac{\varepsilon - \varepsilon_0}{\varepsilon_0} P}$$

or

$$\frac{3}{4\pi} \cdot \frac{\nu_r^2 - 1}{\nu_r^2 + 2} = \frac{N' v(\varepsilon_r - 1)}{4\pi + (\varepsilon_r - 1)P}; \qquad \nu_r = \frac{\nu}{n_0}; \qquad \varepsilon_r = \frac{\varepsilon}{\varepsilon_0}.$$

The expression is entirely analogous to that for a vacuum. We need merely substitute ν_r for ν and ε_r for ε.

In case the light vector is not parallel to the axis, we introduce the relative main polarizabilities h and h'.

If the relative optical dielectric constant is $\mu_r^2 = \frac{\varepsilon}{\varepsilon_0}$, and if the material is isotropic, it follows that

$$h = \frac{(\mu_r^2 - 1)}{4\pi + (\mu_r^2 - 1)P}; \qquad h' = \frac{(\mu_r^2 - 1)}{4\pi + (\mu_r^2 - 1)P'}.$$

If the material is anisotropic, and if the main axes coincide with the ellipsoid axes, we can write

$$h = \frac{(\mu_r^2 - 1)}{4\pi + (\mu_r^2 - 1)P}; \qquad h' = \frac{(\mu_r'^2 - 1)v}{4\pi + (\mu_0'^2 - 1)P'}$$

where μ_r^2 and $\mu_r'^2$ are the complex main dielectric constants.

We now regard the medium as a system of induced dipoles with the relative polarizability h and h'. If the electric field of the light vector has the magnitude E_0, the particle will be acted upon by a field $E = E_0\left(1 + \frac{4\pi}{3}\varkappa\right)$, where $\varkappa$ is the relative optical susceptibility of the solution.

For the electrical moment in the directions 1, 2, 3, we obtain

$$f_1 = h E_1 v$$
$$f_2 = h' E_2 v$$
$$f_3 = h' E_3 v$$

If the light passes along the y-axis, we obtain for the two other axes

$$f_z = [h E_1 \cos(1, z) + h' E_2 \cos(2, z) + h' E_3 \cos(3, z)] v$$
$$f_x = [h E_1 \cos(1, x) + h' E_2 \cos(2, x) + h' E_3 \cos(3, x)] v.$$

The mean polarization of the solution in the different directions will then be

$$\frac{F_z}{E_z} = N' v \int [h' + (h - h') \cos^2(1, z)] F \, d\Omega$$

$$\frac{F_x}{E_x} = N' v \int [h' + (h - h') \cos^2(1, x)] F \, d\Omega$$

and finally, by introducing the Euler angles

$$\frac{F_z}{E_z} - \frac{F_x}{E_x} = N' v (h - h') \int\int [\cos^2\theta - \sin^2\theta \cos^2\varphi] F \sin\theta \, d\theta \, d\varphi .$$

The optical susceptibility, in a direction i of the space fixed coordinates, is

$$\varkappa_i = \frac{(\varepsilon_i' - 1)}{4\pi}; \quad \varepsilon_i' = \varepsilon_i / \varepsilon_0.$$

We thus obtain:

$$\varkappa_z - \varkappa_x = \frac{1}{4\pi}(\varepsilon_z' - \varepsilon_x') = \frac{\nu_z'^2 - \nu_x'^2}{4\pi} = \frac{F_z}{E_z} - \frac{F_x}{E_x}; \quad \nu' = \frac{\nu}{n_0}$$

$$\nu_z'^2 - \nu_x'^2 = 4\pi N' v (h - h') \int\int (\cos^2\theta - \sin^2\theta \cos^2\varphi) F \sin\theta \, d\theta \, d\varphi =$$

$$= 2\pi N' v (h - h') \Big[6\pi \int_{+1}^{-1} \cos^2\theta \, F \, d(\cos\theta) - 1 \Big].$$

For the purpose of simplification, we now put

$$U = \int_{-1}^{+1} e^{\gamma x^2} dx; \quad \gamma = \frac{v H^2}{2 k' T} (k_1 - k_2)$$

and then find that the integral is the following mean value of $\cos^2\theta$

$$\overline{\cos^2\theta} = 2\pi \int_{-1}^{+1} \cos^2\theta \; F \, d(\cos\theta) = \frac{1}{U} \cdot \frac{dU}{d\gamma}.$$

The course of the double refraction can then be described with a Langevin function. For small values of γ, the following development in series can be made:

$$\nu'^2_z - \nu'^2_x = 4\pi N' v (h-h') \left(\frac{\gamma}{15} + \frac{2\gamma^2}{315} + \cdots \right).$$

The linear part leads to

$$\nu'^2_z - \nu'^2_x = \frac{4\pi}{15 k' T} H^2 N' v^2 (k_1 - k_2)(h-h').$$

Now $\nu = n(1 - ki)$ where n is the real refractive index and k the absorption index.

Distinguishing real and imaginary quantities, we obtain with some approximations

$$n_z - n_x = \frac{2\pi n_0}{15} \frac{N' v^2}{k' T} (k_1 - k_2) H^2 (h-h')^{\text{Real}}$$

$$-n_z^2 k_z + n_x^2 k_x = \frac{2\pi n_0}{15} \frac{N' v^2}{k' T} (k_1 - k_2) H^2 (h-h')^{\text{Imag.}}.$$

The expression for $h-h'$ can in general be written in the following way (see Snellman and Björnståhl (43)).

$$h-h' = \frac{3v}{4\pi n_0^2} \left\{ \frac{3[m^2(1-\varkappa^2) - m'^2(1-\varkappa'^2) - 2i(\varkappa m - \varkappa' m')] + }{\left\{ 3 + \gamma \left[\frac{m^2}{n_0^2}(1 - \varkappa^2 - 2\varkappa i) - 1 \right] \right\} \cdot} \right.$$

$$\frac{+ (\gamma' - \gamma) \left[\frac{m'^2 m^2}{n_0^2} (1 - \varkappa^2 - 2\varkappa i)(1 - \varkappa'^2 - 2\varkappa' i) - \right.}{\cdot \left\{ 3 + \gamma' \left[\frac{m'^2}{n_0^2}(1 - \varkappa'^2 - 2\varkappa' i) - 1 \right] \right\} +}$$

$$\left. \frac{- m^2(1 - \varkappa^2 - 2\varkappa i) - m'^2(1 - \varkappa'^2 - 2\varkappa' i) + n_0^2 \right]}{+ 0}$$

where m and m' are the real refractive indexes of the particle and $\varkappa$ and $\varkappa'$ are the absorption indexes and

$$\gamma = \frac{3P}{4\pi}; \quad \gamma' = \frac{3P'}{4\pi}$$

where P and P' are form factors connected with the optical ellipsoid axes according to the relation given on page 54.

In regard to dyes, let us now make the presumably correct assumption that their own anisotropy greatly predominates over the anisotropy in shape. Let us further assume that the absorption takes place mainly in one direction.

With a view to further simplification, let us further assume that $m = n_0$, i. e. that the solvent has approximately the same refractive index as the particle in the direction where the absorption is small.

For $\varkappa = 0$; $m = n_0$, we then obtain with $a' = m'^2(1 - \varkappa'^2) - m^2$

$$[h-h']^{\text{Real}} = -\frac{3v}{4\pi}\left\{\frac{3n_0^2 a' + \gamma'(a'^2 + 4\varkappa'^2 m'^3)}{(3n_0^2 + \gamma' a')^2 + 4\gamma'^2 \varkappa'^2 m'^4}\right\}$$

$$[h-h']^{\text{Imag.}} = \frac{3v}{4\pi}\left\{\frac{2\varkappa' m'[3n_0^2 - \gamma' a'(m'-1)]}{(3n_0^2 + \gamma' a')^2 + 4\gamma'^2 \varkappa'^2 m'^4}\right\}.$$

If we put $\varkappa' = 0$, $m' = n_0$, we obtain the same equations, but with opposite signs, when γ, m, a is introduced instead of γ', m', a'.

These formulas can now be used for computing the dispersion of the double refraction and the amplitude effects in dyes.

For long rod-shaped particles we have $\gamma = 0$, $\gamma' = 3/2$.

When the absorption normally to the longitudinal direction of the particle is largest, we obtain

I a)

$$[h-h']^{\text{Real}} = -\frac{v}{4\pi}\left\{\frac{a'(n_0^2 + a'/2) + 2\varkappa'^2 m'^3}{(n_0^2 + 1/2\, a')^2 + \varkappa'^2 m'^4}\right\}$$

$$[h-h']^{\text{Imag.}} = \frac{v}{4\pi}\left\{\frac{2\varkappa' m'[n_0^2 - \frac{a'}{2}(m'-1)]}{(n_0^2 + 1/2\, a')^2 + \varkappa'^2 m'^4}\right\}$$

and when the absorption along the major axis of the particle is largest

I b)

$$]h-h']^{\text{Real}} = \frac{v}{4\pi}\frac{a}{n_0^2}$$

$$[h-h']^{\text{Imag.}} = -\frac{v}{4\pi}\frac{2\varkappa m}{n_0^2}.$$

For thin disciform particles we have $\gamma = 3$, $\gamma' = 0$ and similarly

II a)

$$[h-h']^{\text{Real}} = -\frac{v}{4\pi}\frac{a'}{n_0^2}$$

$$[h-h']^{\text{Imag.}} = \frac{v}{4\pi}\frac{2\varkappa' m'}{n_0^2}$$

II b)

$$[h-h']^{\text{Real}} = \frac{v}{4\pi}\left\{\frac{a(n_0^2+a)+4\varkappa^2 m^3}{(n_0^2+a)^2+4\varkappa^2 m^4}\right\}$$

$$[h-h']^{\text{Imag.}} = -\frac{v}{4\pi}\left\{\frac{2\varkappa m[n_0^2-a(m-1)]}{(n_0^2+a)^2+4\varkappa^2 m^4}\right\}.$$

If a (resp. a') is positive, the real and the imaginary part will have different signs. Case II b) can scarcely be an exception, as the figures then have excessive values for the refractive index.

If a (resp. a') is negative and $\varkappa$ is great, the real and imaginary parts will have the same signs in cases I b) and II a). In case I a) the real part is usually negative, the imaginary part positive. In case II b) the real part is positive, the imaginary part negative.

In cases of anomalous dispersion, a (or a') may be positive in one part of the spectrum and negative in another, according as $m'^2(1-\varkappa'^2) \gtrless m^2$.

The double refraction may thus likewise have different signs in different parts of the spectrum.

The sign of the measured magnetic double refraction will, of course, be the same as that for the expression $(k_1-k_2)(h-h')$.

The formulae also indicate that Zocher's rule is not quantitatively applicable. The maximum in the amplitude effect and the inversion of the double refraction in the dispersion curve may very well be shifted in relation to one another.

If there are two different places along the wave-length scale, where changes in the double refraction are indicated, each of these places must correspond to a part, where we have anomalous dispersion of the refractive index.

For a quantitative interpretation of the formulae, it is necessary to know the refractive index and absorption coefficients of the dyes. Unfortunately, such determinations have been very sparse, and the author has been unable to find in the literature any such values for the dyes dealt with below.

Measurements.

As the dyes are intensily absorbing, thin cuvettes must be employed. In the author's experiments therefore cuvettes 1, 2 and 5 mm thick were used.

Aniline blue was dissolved in alcohol and diluted to a strong aqueous sol. It was precipitated with NaAc, filtered-off, washed with water and dried.

The sols where then produced by pouring a concentrated solution of aniline blue, dissolved in alcohol, into water, whilst stirring. If low concentrations of the aniline solution were used, sols which showed only a slight double refraction were obtained. If sols were produced with higher concentrations of aniline blue, we obtained sols which in the magnetic field showed marked anisotropy even when diluted. It took some time before the sols had completely developed in the stock solutions. The dependence of the double refraction on the field strength varied somewhat with the way in which the sols were prepared. In most cases we obtained a double refraction increasing as the square of the field strength. In some cases with more concentrated stock solutions a tendency towards saturation was observed.

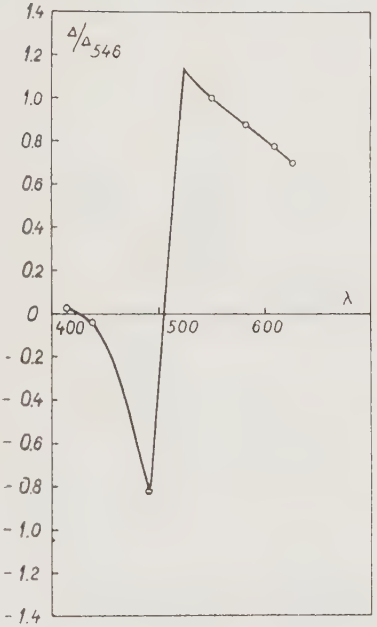

Figure 27. Relative dispersion of Magnetic double Refraction in Aniline Blue Colloid. Aqueous Solution. Double Refraction for $\lambda_0 = 546$ mμ is equalized to one.

It will be seen from the figure that the dispersion is markedly anomalous, as had already been found by Zocher. The double refraction is positive in red, but after a sudden change at about 500 mμ becomes negative and then again gradually passes into a positive double refraction (at about 400 mμ). The dispersion seems, broadly speaking, to be independent of the concentration,

Table XI.

Aniline Blue.

Dispersion of Double Refraction in Aqueous Solution.

$H = 10\,000$ Oe. $L = 1$ cm.

λ_0 mμ	Concentration					
	1.15 10^{-5} g/l		4.8 10^{-4} g/l		2.5 10^{-3} g/l	
	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}
623	+ 8.0	+0.77	+30.5	+0.71	+159	+0.711
608	+ 8.8	+0.78	+34	+0.79	+178	+0.80
578	+10.0	+0.88	+37.9	+0.88	+197	+0.88
546	+11.3	+1	+43	+1	+223	+1
492	− 9.1	−0.86	−34.4	−0.80	−179	−0.80
438	—	—	− 1	−0.02	− 4	−0.02
408	+ 1	+0.08	+ 4	+0.09	+ 18	+0.08

Amplitude Effect.

$c = 2.5\ 10^{-3}$ g/l

λ_0 mμ	$(a_{\parallel}/a_{\perp}-1)\,10^3$
608	+ 17.4
578	+ 35
546	+102
492	+ 30
438	+ 5.8

Dispersion in Benzene Solution.

λ_0 mμ	Δ'	Δ/Δ_{546}
608	+4° 12′	+0.99
578	+3° 58′	+0.97
546	+4° 16′	+1
492	+4° 35′	+1.10
438	+5° 16′	+1.32

and the general course agrees well with what might be expected according to the theory given for particles with anomalous dispersion of the refractive index and intense absorption in one direction.

The amplitude effect was positive (i. e. the greatest absorption in the direction parallel to the field) and showed a high maximum at about 500 mμ.

In streaming double refraction experiments the particles show the same dispersion curve, but with opposite signs. It may therefore be assumed that the particles, which apparently are long rods, adjust themselves normally to the field, which is in fact to be expected for diamagnetic particles.

Attempts were made to prepare an aniline blue suspension in benzene. A solution of aniline blue in amyl alcohol was poured

into benzene, whilst stirring. This solution gave a double refraction which rapidly proceeded to saturation. In the whole range of wave-length investigated the double refraction was positive. In this colloidal suspension the anomalous dispersion had disappeared.

Some values from the measurements of aniline blue are given in table XI on page 62.

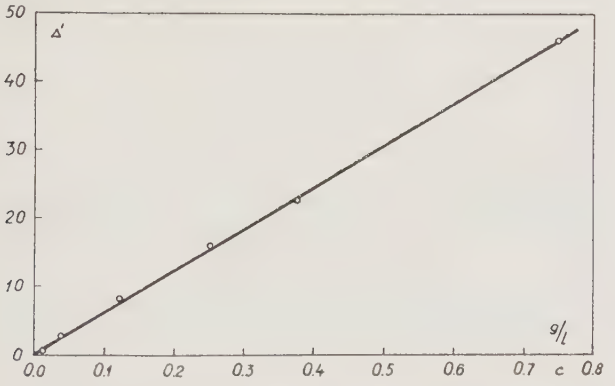

Figure 28. Alizarin Sodium Sulfonate. Variation of Double Refraction with Concentration. ($\lambda_0 = 546$ mμ.)

Alizarin sodium sulfonate directly dissolved in water, showed a positive double refraction. It rapidly proceeded to saturation with the field. The saturation usually set in by a value of $H = 17 \cdot 10^3$ Oe. At the concentrations measured (up to $c = 0.75$ g/l) the dependence on the concentration was a linear function of the phase difference (figure 28). The dispersion, as shown in figure 29, was marked and independent of the concentration.

In *Pinachrome* we found a negative effect, which, at the concentrations tested (0.1—0.6 g/l) proceeded very rapidly as the field increased to saturation. The double refraction was great in the violet, blue and green range of the spectrum but decreased rapidly in the yellow and red part of the spectrum. Figure 30 shows the dispersion curve. The amplitude effect was positive. The addition of salt did not modify the effects, which were here found to be independent of concentration.

Alizarin cyanin showed a positive double refraction. The birefringence is smaller in the violet range of the spectrum but

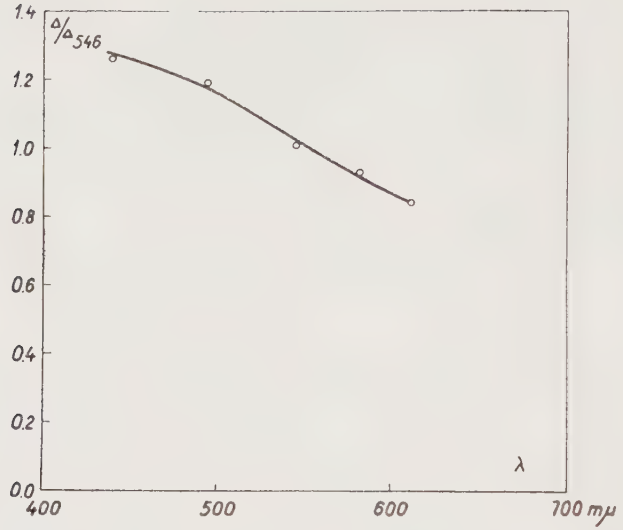

Figure 29. Alizarin Sodium Sulfonate. Relative Dispersion of Double Refraction with Wave-length. Double Refraction for $\lambda_0 = 546$ mμ is equalized to one.

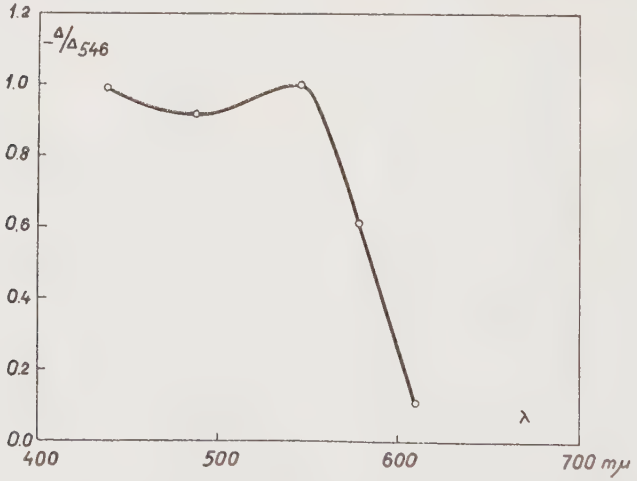

Figure 30. Pinachrome. Relative Dispersion of Double Refraction with Wave-length. Double Refraction for $\lambda_0 = 546$ mμ is equalized to one.

increases rapidly with the wave-length. The rather great negative dichroism passed through a maximum at 550 mμ. The dispersion of the effects were independent of the concentration in the measured range. For the effects see figures 31—32.

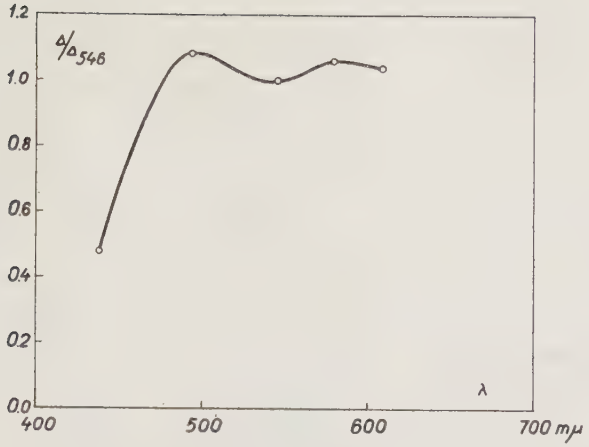

Figure 31. Alizarin Cyanine. Relative Dispersion of Double Refraction with Wave-length. Double Refraction for $\lambda_0 = 546$ mμ is equalized to one.

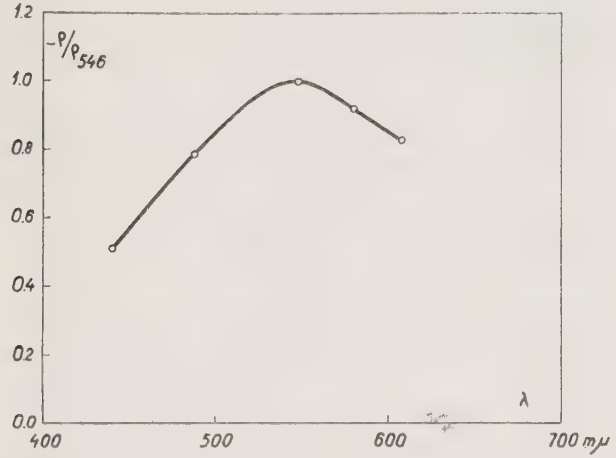

Figure 32. Alizarin Cyanine. Relative Dispersion of Amplitude Effect with Wave-length. Amplitude Effect for $\lambda_0 = 546$ mμ is equalized to one.

These substances thus showed, in aqueous solutions, effects in agreement with the theory.

In aqueous solutions of *Azoblue* the results were somewhat different. At lower concentrations the effect changed with the square of the field strength, at higher concentrations saturation phenomena were observed. The dependence on the concentration was not linear: the double refraction increased, at first rapidly

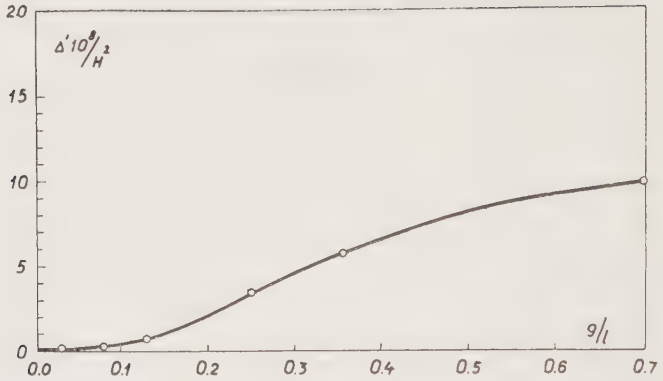

Figure 33. Azoblue. Variation of Double Refraction with Concentration. ($\lambda_0 = 546$ mμ).

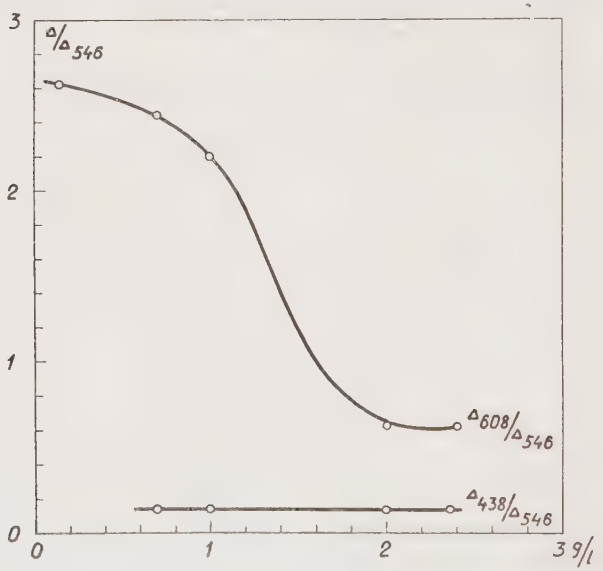

Figure 34. Azoblue. Relative Dispersion of Double Refraction by Different Concentrations. Double Refraction for $\lambda_0 = 546$ mμ is equalized to one.

and then slower with the concentration, when a certain minimum concentration had been exceeded (figure 33). At the red end of the spectrum the dispersion rapidly changed with the concentration, the double refraction decreased. In the violet range it remained practically unchanged (figure 34).

The double refraction was dependent on the salt concentration. Here too it increased with the square of the field strength in low concentration of azoblue. The anisotropy reached a maximum after a certain increase in the salt concentration. It was attained at 0.2 mol NaCl in the case when we had 0.0062 g/l azoblue in the solution (figure 36). In this case too the dispersion ratio in red changed in the same manner as before, whereas, when the salt concentration exceeded 0.2 mol NaCl it appeared to be constant (figure 35).

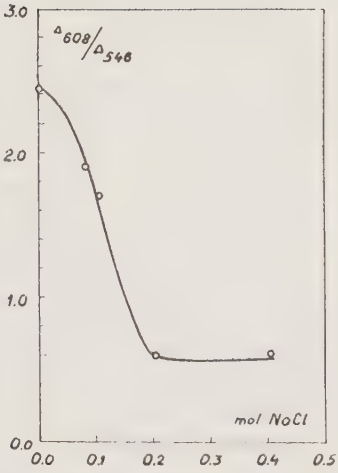

Figure 35. Azoblue. Relative Dispersion of Double Refraction for Concentration 0.062 g/l in different Sodium Chloride Solutions. Double Refraction for $\lambda_0 = 546$ mμ is equalized to one.

The amplitude effect in these solutions could not be followed with the dilution. It was found to be too small to permit any reliable results. They have therefore not been reported here. However, we can state that in the red part

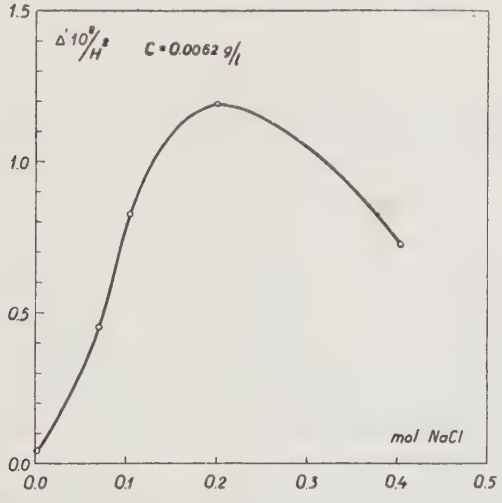

Figure 36. Azoblue. Variation of Double Refraction with Concentration of Sodium Chloride in the Solution. Concentration of Azoblue 0.0062 g/l.

Table XII.

Azoblue.

Dispersion of Double Refraction. Aqueous Solution.

$\lambda_0 m\mu$	Concentration									
	0.125 g/l		0.7 g/l		1.0 g/l		2.0 g/l		2.38 g/l	
	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}
608	+2.66	+2.66	+24.2	+2.42	+41.6	+2.19	+40.5	+0.60	+48	+0.60
578	+1.60	+1.60	+15.7	+1.57	+29.4	+1.55	+67	+0.98	+78	+0.98
546	+1.0	+1	+10.0	+1	+19.0	+1	+68	+1	+80	+1
492	—	—	− 2	−0.2	− 4	−0.2	− 4	−0.6	− 5	−0.7
438	+0.1	—	+ 1.4	+0.14	+ 3	+0.15	+10.5	+0.15	+12	+0.15

Salt Solution.

$c = 0.062$ g/l Azoblue.

λ_0 mμ	Mol. NaCl/l							
	0.07		0.1		0.2		0.4	
	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}	Δ'	Δ/Δ_{546}
608	+23.5	+1.90	+28	+1.77	+ 5.8	+0.58	+4.5	+0.60
578	+18	+1.50	+25.2	+1.44	+ 9.8	+0.98	+6.5	+0.87
546	+12	+1	+17.5	+1	+10.0	+1	+7.5	+1
438	+ 2	+0.17	+ 2.8	+0.16	+ 1.6	+0.16	+1	+0.14

Amplitude Effect.

$c = 1.0$ g/l Azoblue.

λ_0 mμ	Aqueous solution	0.1 m NaCl
	$(a_{\parallel}/a_{\perp}-1)\,10^3$	$(a_{\parallel}/a_{\perp}-1)\,10^3$
608	−19.8	−14
578	+35.0	+23.8
546	+44.2	+32.6
492	+52.0	+44.0
438	+25.8	+11.6

of the spectrum this effect in dilute solutions was positive in concentrated negative.

In table XII some measurements are given for azoblue.

Chrysophenine was examined in some concentrations. Here the double refraction, after a threshold value, rose very rapidly with

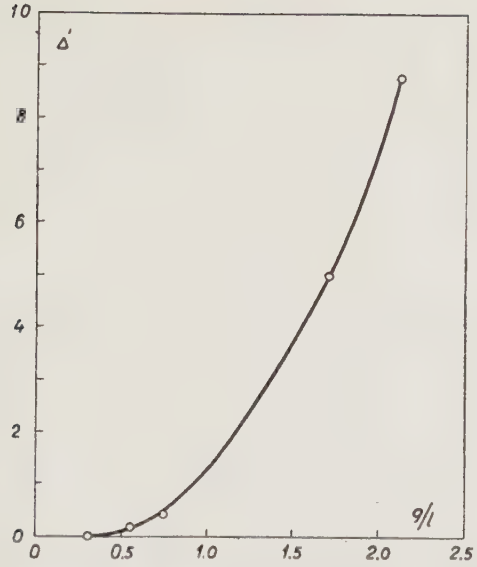

Figure 37. Chrysophenine. Variation of Double Refraction with Concentration ($\lambda_0 = 546$ mμ).

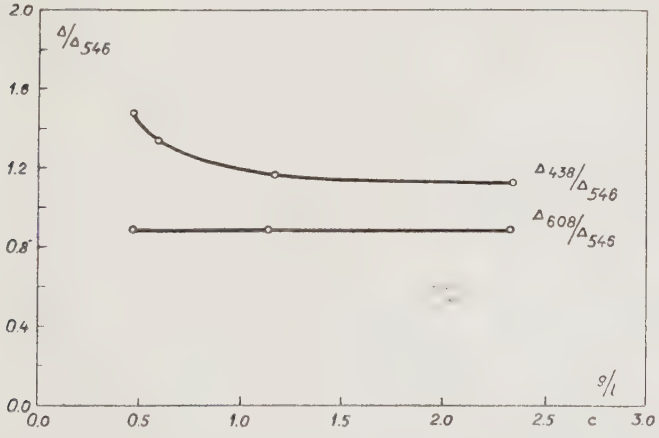

Figure 38. Anthracene Blue. Relative Dispersion of Double Refraction with Concentration. Double Refraction for $\lambda_0 = 546$ mμ is equalized to one.

the concentration (figure 37). Owing to the very intense absorption, the dispersion of the double refraction could be measured only in green to red. In this range the dispersion was very small and independent of the concentration.

In *Anthracene blue* anomalies of the same type as by azoblue were observed in the violet range of the spectrum. At the red end of the spectrum the dispersion was practically constant. The dependence of the dispersion ratio $\Delta_{438}/\Delta_{546}$ and $\Delta_{608}/\Delta_{546}$ is shown in figure 38. The double refraction is here positive.

Discussion.

The tentative measurements given above, were started in order to gain some information about the magnetic double refraction of some dye-stuffs. Thus it might be possible use them for studying the structure of other colloids.

The anomalous dependence on concentration of the dispersion in azoblue and some other dye-stuffs shows that one must collect more information of the structure of dye-stuff colloids before being able to use them as indicators in studying the structure of other colloids. One may also in this connection ask if all the studies, using dye-stuffs as indicators to gain information about fibres, are quite correct.

It is evident that in azoblue coarse grained material is in equilibrium with more fine-dispersed material. This equilibrium is probably reversible, because, on diluting a concentrated solution, similar results were obtained as in the case when a solution was directly prepared with the same concentration. The time required for the establishment of equilibrium was evidently quite short, — to judge by the determinations, less than four minutes.

The forces which act in the formation of the micelles arrange the molecules in a regular way. Without such regularity, a magnetic anisotropy could scarcely develop at all. From the magnetic tests and the qualitative investigations of the streaming double refraction, it may be inferred that the elongated particles, which we have in the cases where we know something about the shape, adjust themselves with their major axis at right angles to the magnetic field. We therefore find the greatest diamagnetism along this axis. With this knowledge of the magnetic axis, and with our experience of the magnetic anisotropy of the benzene nucleus, it may be concluded that the molecules in the micelle lie with their ring plane at right angles, or nearly at right angles, to the long axis of the micelle.

The general view is that no changes in the dispersion with the concentration are to be expected. In some cases changes in the dispersion have been observed in different preparations of the same kind of colloids (Björnståhl (44)). They have been attributed to modifications of the size of the particles in the solution.

In the author's investigations, however, the changes in dispersion with the concentration have been found to be so marked that, stated from our theory, they cannot possibly be attributed merely to modification in the shape. The dependence of the anomalous dispersion on the concentration must therefore be ascribed to radical changes in the very structure of the particles.

From the works of Scheibe (45) and others, we now know a number of dyes, chiefly of the type of pseudoisocyanine and pinacyanol, where the intensity of the absorption band, though not its position, is modified by micellar formation, which, moreover, gives rise to new absorption bands.

We must count, generally speaking, with two kinds of forces in these micellar formations, firstly dispersion forces, which act among the hydrophobe hydrocarbon residues, and second electrostatic forces, proceeding from ions or dipoles.

The tests with aniline blue indicate that the double refraction may undergo changes when the forces which build up the particle are modified. Aniline blue in benzene shows a quite normal dispersion in visible light, whereas in aqueous solutions the double refraction suddenly changes in a marked degree at about 500 mμ.

In benzene we may expect a greater affinity between the hydrocarbon residues and the solvent. In this case the particles are built up with polar forces, in quite a different manner than in water, where the polar groups have greater affinity to the water molecules than to the hydrocarbon residues. In the water the micelle is built up by the dispersion forces acting on the hydrocarbon residues. These dispersion forces greatly affect the electron paths, which are particularly sensitive to interferences due to the action of light.

In this connection it is interesting to note that our results, according to which we find an intense absorption along one axis

of the particle, indicate that we are concerned with anisotropic resonators connected with the chromophore group.

W. Kuhn (45) expresses the view that in complicated molecules (or micelles), owing to interaction between the different parts, we may usually expect anisotropy in the resonators. A satisfactory explanation of this phenomenon, on the basis of the quantum theory, seems, however, to be lacking. This is evidently due to difficulties in defining the inner fields and in specifying the type of resonators.

The importance of the inner fields for these resonators is indicated, in our investigations, by the behaviour of aniline blue as well as by the way in which the dispersion was found to vary with the concentration, in tests on certain other dyes.

In azoblue, which was studied somewhat more thoroughly, in aqueous solution, the dependence of the dispersion on the concentration is clearly marked. In the more dilute solutions it approaches $\Delta_{608}/\Delta_{546} = 2.65$, in the more concentrated solutions it falls to a value of the magnitude of 0.6. The dispersion $\Delta_{438}/\Delta_{546}$ seems to be constant and has the value 0.2. In the last case, however, the light flux according to the absorption as well as the sensibility of the eye are both so small that the determinations may show a great error.

Whether the double refraction changes with the concentration to the same extent as the dispersion could not be determined. For, at the higher concentrations the double refraction rapidly proceeded to saturation, so that a basis for comparison with the concentrations, where a quadratic effect was observed, could not be obtained.

Still more marked is this effect in salt solutions. If the curve for the change in dispersion with salt concentration is compared with the corresponding curve for the change in double refraction, it will be found that the dispersion changes as the double refraction increases, whereas in the concentration, where salting out effects set in, the dispersion appears to be constant.

Kortüm (47) and Scheibe (45) have found in investigations of the absorption of some other dyes that they could attribute one sort of absorption to particles with a small number of molecules and another to particles which contain a great number of molecules. In the same manner we can attribute a dispersion of the

double refraction to particles which contain a small number of molecules and another to particles which contain a great number of molecules.

As we can see from the measurements, the change between the two types of particles in the solution does not rapidly set in when the concentration increases.

We are not yet able to say much about the state which causes the differences between the two types of particles.

In another investigation Snellman and Björnståhl (43) suspected that p-azoxyphenetole was in a nematic form in aqueous suspension. This substance is highly dichroitic in this state but in the real crystalline state the dichroism does not appeare.

It seems therefore probably in the last cases here investigated that we have nematic aggregates in the more concentrated solutions.

Summary.

Some measurements of the field for different types of pole shoes of the electromagnet at Upsala have been performed.

The Cotton-Mouton constants of some calibration liquids in refined state have been measured. A new value for the nitrobenzene has been given. The author's values for benzene and toluene agree with the values given by Matull and Szivessy. Some anomalies at purification are observed. The variation of the Cotton-Mouton constant with wave-length in the visible range of the spectrum has been investigated.

Measurements of the magnetic double refraction clearly show that in hydrotropic solutions association takes place between the hydrotropic salt and the soluble substance.

For solutions of dyes a theory is given on the variation of the double refraction with the wave-length. The double refraction is in the theory connected with the material constants and the shape of the particle. A new dependence of the variation with the wave-length of the magnetic double refraction on the concentration is found for some dyes.

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